

Dispersion Characteristics of Montmorillonite, Kaolinite, and Illite Clays in Waters of Varying Quality, and Their Control with Phosphate Dispersants

By B. N. ROLFE, R. F. MILLER, *and* I. S. McQUEEN

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

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SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

DISPERSION CHARACTERISTICS OF MONTMORILLONITE, KAOLINITE, AND ILLITE CLAYS IN WATERS OF VARYING QUALITY, AND THEIR CONTROL WITH PHOSPHATE DISPERSANTS

By B. N. ROLFE, R. F. MILLER, and I. S. McQUEEN

ABSTRACT

This study is concerned with the dispersion characteristics of montmorillonite, kaolinite, and illite clay minerals in waters of different hardness and the relation of these characteristics to the control of canal seepage by artificial sedimentation. The effect of dehydrated sodium phosphates on dispersion was also investigated. The importance of recognizing colloidal suspensions as ternary systems (colloid, water, ionized salt) is emphasized.

Representative samples of montmorillonite, kaolinite, and illite clays, were saturated with either calcium or sodium and then prepared as 1 percent suspensions in distilled, hard, and soft waters. This provided extreme clay-water environments with respect to an investigation of the control of dispersion through the injection of sodium polyphosphate-type dispersants. Intermediate conditions were also provided by using a water of intermediate quality between hard and soft extremes. A native montmorillonite clay was selected for use as the prototype of calcium-sodium exchange relation and was replicated on the kaolinite and illite clays. The dispersion characteristics of the clay minerals under the preceding environments are involved in sediment transport in natural streams and play a decisive role in sediment-lining procedures. The deflocculents used in the investigation were sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), sodium hexametaphosphate ($\text{Na}_6\text{P}_6\text{O}_{21}$), and sodium hexametaphosphate plus soda ash (Na_2CO_3) in a 50-50 by weight mixture. The deflocculents varied in dispersion efficiency depending upon the interaction of the clay-water-phosphate systems. These variations were related to dissociation of sodium and length of polymer chains. A specific deflocculent for each clay, water, ionized salt system was indicated by the data.

The percentage of dispersion was measured by sensitive hydrometers, reading from 0-10 grams of colloid per liter. This instrument gave generally acceptable results, except where conditions did not conform to the limitations imposed by basic theories of hydrometer analysis. The greatest source of trouble was in montmorillonite suspensions which produced anomalous increases in the hydrometer readings. This was attributed to consolidation of uniformly sized particles in the hydrometer jar, producing a greater apparent specific gravity in the zone measured by the hydrometer. The increase was usually accompanied by phenomena similar to gelation.

As an aid in comparing the many hydrometer analyses (consisting of 3,156 hydrometer readings), the index of dispersion concept was introduced. This value totals selected ordinates under a dispersion curve and compares the sum to a base value obtained by the same method for selected ordinates under a standard curve representing sodium-saturated clays in distilled water. Thus,

for each clay mineral there is a standard value against which all deflocculating treatments may be compared.

The results indicate the importance of understanding the chemistry of the ternary system (clay, water, ionized salt). The dependence of dispersion on the interaction of these three factors is great. Each clay-mineral group has specific properties and characteristics in the system. Not only does montmorillonite show the greatest colloidal yield but it is the most responsive to changes in chemical environment. It is far more difficult to sodium saturate a calcium clay than a hard calcium water. Although repulsion between like negative surfaces is the basis of dispersion, the location, source and amount of negativity of the various clay minerals determine the best deflocculent for effecting dispersion.

The general implications of the study have a bearing on several fields of sedimentation. With respect to sediment lining of canals, the investigation indicated the relative superiority of montmorillonite-type clays for the penetration and filling of small voids. With respect to filling of joints, cracks, burrows, and other relatively large openings, kaolinite and illite clays may be suitable as mortaring agents.

INTRODUCTION

Irrigation is practiced in areas where precipitation is insufficient to produce a profitable crop. It is also used to a limited extent where supplemental applications of water are needed to offset irregularities in rainfall distribution. More than 100 million acre-feet of water is diverted annually for irrigation purposes in the 17 Western States (exclusive of Alaska). The amount of water that reaches the user is reduced during transport by a minimum of 25 percent (Dirmeyer, 1955). Most of this loss may be attributed to seepage from unlined canals. In addition to the actual decrease in available water supply, there is the problem of damage to cropland adjacent to seeping irrigation canals, such as waterlogged soil, drowned crops, and zones of salt accumulation. Investigation has therefore been centered on possible means of decreasing the losses.

Canal seepage has been diminished by treating the leaking bed material to reduce its permeability. These treatments consist of lining the canals with materials

such as concrete, plastics, bentonite, and asphalt membranes, and compacted earth. The cost of such treatment ranges from \$0.15 to \$5 per square yard of canal bed. None of these treatments has satisfactorily supplied a low-cost canal lining. Sediment lining seems to offer great promise, and the present investigation is the outgrowth of the need for low-cost canal lining. Canal lining by sedimentation is very appealing because little special equipment is required.

Sediment lining of canals was originally a natural phenomenon connected with the early history of irrigation farming. Irrigation waters were first diverted directly from natural streams. The spring floodflows at the start of the growing season normally carried enough suspended sediment to serve as a natural seepage control through sedimentation. The only drawback to this means of seepage control was its transient stability. Clear irrigation water, diverted during the middle and latter parts of the season broke up the sediment cake and carried it away in suspension. As irrigation progressed the installation of reservoirs as sources of irrigation waters terminated the favorable natural sedimentation of former years by intercepting the sedimenting material.

An artificially introduced sedimenting material should be more stable than the temporary sediment cake of the past. Seepage control by sedimentation probably could be improved, either by increasing the stability or toughness of the filter cake at the surface of the bed material, or by adding a fine-grained sediment below the bed surface as a void filler.

If the sedimenting material is to be used as a void filler below the surface of the canal bed, it should be transportable by the canal water. This imposes certain limits on the size and transportability of the particles. The particles probably should be colloidal in size (less than 1 micron in diameter), and the chemistry of the clay-water system should be controlled so that the particles do not coagulate and form clumps of particles that will not enter the soil voids. A native Wyoming bentonite that apparently conformed to the above requirements was used for sediment lining by the U.S. Bureau of Reclamation on its Kendrick project at Casper, Wyo. This was a bentonitic clay that had a median particle diameter of 0.5 micron.

It was found early in the work at Kendrick, however, that this bentonite was equally responsive to both flocculating and dispersing environments. If the canal waters were of such a chemical quality as to promote floc formation, the transport of the introduced sedimenting material was shortlived. The bentonite suspension failed to cover the desired extent in the canal because the particles generally precipitated a short distance from the starting point. Also, flocs of

bentonite with a sedimentation diameter larger than the desired 0.5 micron were formed; these would not penetrate the voids of canal-bed material.

There seemed to be a need for a dispersing medium or chemical control to insure the suspension of bentonite in differing canal waters. It was at this stage in the sediment-lining investigation that the Geological Survey was approached on the subject of a possible cooperative project with Colorado Agricultural and Mechanical College.

The transport of sediment by water may be influenced by the kind of sediment and the chemical quality of the water. Therefore a basic study into the dispersion characteristics of several clay minerals in waters of differing chemical quality was of mutual interest to the Geological Survey and to investigators into canal lining by sedimentation.

The need for chemical additives to maintain a dispersion medium led to discussions with representatives from chemical companies. The several phosphate deflocculents available seemed to offer the greatest promise of success so the study was designed to investigate these in conjunction with the ternary system (clay, water, ionized salt).

PERSONNEL

The investigation was made by the Geological Survey in cooperation with Colorado Agricultural and Mechanical College, now Colorado State University. The investigation was started in 1954 at Colorado Agricultural and Mechanical College, where laboratory space was provided for the Geological Survey, and was completed in 1956 in the soils laboratory of the Geological Survey at the Denver Federal Center. The investigation by Geological Survey personnel was under the administrative direction of R. W. Davenport, chief Technical Coordination Branch succeeded by C. C. McDonald, chief General Hydrology Branch, and under the supervision of H. V. Peterson, project hydrologist and later branch area chief, General Hydrology Branch, Denver, Colo.

B. N. Rolfe, soil scientist, was in immediate charge of the investigation until his resignation in 1956. Reuben F. Miller, soil scientist, and I. S. McQueen, hydraulic engineer, assisted in the research and completed the report.

ACKNOWLEDGMENTS

There were many formal and informal conferences during the study. The names that follow are those of people who contributed much to the study but any omissions do not imply lesser contributions by others to the overall problem. The writers are indebted to many faculty members at Colorado State University, espe-

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Several chemical companies were generous with time, data, and suggestions. Representing the companies were R. P. Gates, Victor Chemical Works; Clark Sumner, A. R. Maas, R. N. Thompson and W. C. Bennett, Calgon, Inc.; and John Deming, L. V. Sherwood and R. A. Ruehrwein, Monsanto Chemical Co. These men contributed very helpful counsel and furnished supplies of deflocculents for the testing program.

The clay companies were also generous with time, data, and samples. Paul Bechter, American Colloid Co., supplied samples as well as technical information. Messrs. S. C. Lyons and R. E. Lehman of Georgia Kaolin Co. helped by furnishing pertinent data on the kaolin used in the investigation. For the Baroid Co., Messrs. Huebotter, Neznayko, Weintritt, and the late F. J. Williams offered technical advice and information on many aspects of the study.

The writers also wish to acknowledge the fine cooperation given by Engineering Laboratories Division of the U.S. Bureau of Reclamation at Denver, Colo. Messrs. Hunter, Jones, Mielenz, and the late M. E. King were always gracious in exchanging ideas and information during the course of the investigations.

MATERIALS

CLAY MINERALS

The materials used were components of the ternary system; clays, water, and ionizable salts.

The clays used were:

1. Kaolinite, supplied by Georgia Kaolin Co., Dry Branch, Ga.
2. Montmorillonite, trade name "Volclay" supplied by American Colloid Co., Belle Fourche, S. Dak.
3. Illite, an illite-bearing shale from Fithian, Ill.

A discussion of clay mineral properties by B. N. Rolfe is presented on p. 248.

PHOSPHATE DEFLOCCULENTS

Three phosphate deflocculents were selected for the investigation. Each was studied to determine its effect on the control of dispersion in the different clay-water systems utilized in the experiments.

The various phosphates have several common properties, but differ in efficiency as to specific reactions (Chu

and Davidson, 1955; Tchillingarian, 1952; Whitehouse and Jeffrey, 1955; Wintermyer and Kinter, 1955). The results of this investigation indicate only the relative capabilities of three phosphate reagents, all of which were dehydrated sodium phosphates, in dispersing three different types of clay minerals. The chemical composition and general characteristics of the compounds used are given in table 1.

There is apparently some confusion concerning phosphate nomenclature. The terms in this report are those in common usage in the phosphate industry. The term "molecularly dehydrated phosphates" refers to certain complex salts formed by the high temperature dehydration of monosodium orthophosphate, disodium orthophosphate, or an intermediate mixture. The phosphates differ significantly in P_2O_5 content, chemical formula, and atomic arrangement. As is shown in table 1, sodium tripolyphosphate, tetrasodium pyrophosphate, and sodium hexametaphosphate are separate entities and represent distinct phosphate salts with individual, different characteristics.

Table 1 was compiled from literature furnished by Victor Chemical Works and Calgon, Inc. There has been no effort to edit these statements. The writers have merely arranged the information for easy comparative reading.

Sodium tripolyphosphate and sodium hexametaphosphate were used during both years of the study whereas tetrasodium pyrophosphate was used only during the second year. A 50-50 mixture, by weight, of sodium hexametaphosphate and soda ash (Na_2CO_3) was tried during the first year of the study. This was done in response to a suggestion by personnel at Calgon, Inc., on the basis of their experience in the paper industry with dispersing kaolinite clays.

WATERS

The chemical quality of the waters used in the study varied greatly with respect to hardness (calcium, magnesium content). The relative amounts of the metallic ions, calcium, magnesium, and sodium are of paramount importance to the dispersion characteristics of the various clay minerals. Two prototype waters, a hard and a soft water, were selected from a table of representative irrigation waters described in the U.S. Department of Agriculture Salinity Handbook (Richards, and others, 1954). This was in accord with the objective of the work for the first year wherein end-member relations such as sodium- versus calcium saturated clays were to be studied.

The plan for the second year decided upon by interested parties in conferences held at Fort Collins in early 1955 was to study the dispersion characteristics of a clay commercially available in water of intermediate

TABLE 1.—Properties of the phosphate deflocculents used in the study

Deflocculent	Chemical composition	P ₂ O ₅ content (percent)	Physical appearance	Solubility in 100 parts water		Stability to reversion	Sequestration activity	pH of a 1 percent solution	Uses
				Temperature (°F)	Parts				
Sodium tripolyphosphate.	Na ₅ P ₃ O ₁₀ -----	57.8	Powdered, granular.	50 70 160 212	14 15 22 34	10 hr at 100°F solution contains 98 percent sodium tripolyphosphate (unchanged 1.2 percent pyrophosphate, 0.8 percent orthophosphate).	Solubilizes calcium and magnesium.	9.6	Water softening, builder for detergents and soaps, including bar and chip soap (nonblooming), industrial cleaners, dispersant for pitch control in paper manufacture, clay dispersing, textile processing, conditioning drilling mud.
Tetrasodium pyrophosphate.	Na ₄ P ₂ O ₇ (anhydrous).	53.0	-----do-----	50 70 160 212	3 4 14 21	10 hr at 160°F, little hydrolysis, solutions contain 100 percent original tetrasodium pyrophosphate.	Solubilizes magnesium soaps, disperses calcium soaps.	10.2	Water softening, builder for soaps and detergents, conditioning drilling muds, industrial cleaners subjected to high temperature for long periods, stabilizing peroxide bleach baths, clay dispersing, textile processing, de-inking newsprint, tin plating.
Sodium hexametaphosphate.	(NaPO ₃) _n -----	67.0	Glass plates ½-1 inch flat side, ¼-⅓ inch thick.	(¹)	(¹)	To effect complete reversion in solution requires autoclaving with strong acid or strong alkali.	Solubilizes calcium and magnesium soaps, forms soluble complexes with most polyvalent metals.	6.9	Threshold treatment for iron stabilization and corrosion and scale control, water softening, builder for detergents, dispersant for pitch in paper manufacturing, dispersant for clay and pigments, textile and leather processing, conditioner for drilling muds, and processing food products.

¹ Infinitely soluble.

quality. A Wyoming bentonite (Volclay) and water from the Tri-County Canal in central Nebraska, were selected as prototypes for the clays and waters used during the second year's investigation.

Distilled water was the first aqueous medium in which the various clays were dispersed. Any addition of deflocculent to such a clay-water system would merely serve to counter the influence of any hard (Ca^{++} or Mg^{++}) ions in exchange positions on the clay. Under such a premise, a sodium-saturated clay in distilled water should represent maximum dispersion potential, and the dispersion index discussed later is based on this condition.

The composition of the hard water was selected from a field prototype to represent an extreme in flocculating effect. The synthetic model contained the following in milliequivalents per liter: Calcium, 17; magnesium, 8; and sodium, 17. This is an admittedly unusual water because of its high electrolyte content and high calcium, magnesium values. Anions were not regarded as significant during the design stage of this study but proved to be, as will be described later.

The soft water, as with the hard water, was selected from a field prototype to represent the other extreme in waters. The synthetic model contained the following, in milliequivalents per liter: Calcium, 3; magnesium, 2; and sodium, 15.5. This is a highly sodic water and is probably an end member in the range that might be expected in irrigation waters.

Water from the Tri-County Canal in central Nebraska was selected as a prototype for the study because its chemical composition fell midway between those of the hard and soft waters. The synthetic model contained the following, in milliequivalents per liter: Calcium, 6.2; magnesium, 3.6; and sodium, 6.3.

METHODS

WATER SYNTHESIS

The synthetic waters of varying degrees of hardness were assembled in the laboratory by adding the proper amounts of calcium, magnesium, and sodium salts to distilled water. As indicated previously, there was a different experimental procedure for each year of study. This was true for the clays and waters. It is, therefore, convenient to discuss the water synthesis in chronological order.

The analyses of the waters for 1954-55 have been reported in the previous section. Only the sources of the cations are noted here. Sodium was derived from reagent grade sodium chloride (NaCl); calcium from reagent grade calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); and magnesium from reagent grade magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

During the second year (1955-56) the sodium ions were derived from reagent grade sodium chloride. However, to provide calcium, calcium chloride was used instead of calcium sulfate in order to avoid the possible formation of an insoluble precipitate as occurred in the investigation of the hard water.

EXCHANGE COMPLEX SATURATION OF CLAYS

The clay minerals were treated to saturate their exchange complexes with either calcium or sodium or a combination of the two. In the first year's investigation the clay minerals were made homoionic with respect to calcium and sodium. In the second year the clays were ionically adjusted to simulate the exchange complex of a native Wyoming bentonite (Volclay).

Homoionic clays were prepared as follows:

1. 10-gram portions of air-dry clay were placed in 100 milliliter glass centrifuge tubes.
2. 100 milliliters of 1 *N* calcium acetate or sodium chloride were added and mixed with the clay.
3. The centrifuge tubes were placed in beakers containing water and warmed gently overnight on a hot plate.
4. The suspensions were then centrifuged and the supernatant liquid decanted.
5. The above procedure was repeated three times.
6. The clays were washed three times with distilled water, centrifuged and decanted between each washing.
7. The washed clays were transferred into hydrometer jars and filled to 1 liter with the proper aqueous medium.

During the second year's investigation, instead of using homoionic clays, the cation-exchange complex of Volclay was used as a prototype from which calcium-sodium percentages were calculated. As presented in the American Colloid Co. Circular, Data No. 202, the ionic content of Volclay (per 100 grams) is as follows:

	<i>Milliequivalents</i>
Sodium.....	85.5
Calcium.....	22.0
Magnesium.....	1.0
Total.....	108.5

In calculating the percentage of saturation with respect to calcium and sodium, magnesium was grouped with calcium. Therefore, the sodium saturation is equal to $85.5 \div 108.5 \times 100$ or 78.8 percent, and the calcium saturation is 100 percent minus 78.8 percent or 21.2 percent.

The percentage of exchangeable cations was simulated on the kaolinite and illite as follows:

1. Homoionic sodium and calcium clays were prepared as described previously.
2. Instead of transferring the clays to hydrometer jars (step 6), they were air-dried and stockpiled.

3. 7.88 grams of air-dry sodium clay was mixed with 2.12 grams of calcium clay.
4. The mixtures (10 grams) were put into hydrometer jars which were filled to 1 liter with the desired water.

TREATMENT WITH DEFLOCCULENTS

The phosphate deflocculents were added progressively in small increments to each clay-water system to determine the quantity producing the maximum dispersion. The dispersion attained in a phosphate-distilled water medium was considered the maximum obtainable for each type of clay.

The increments of phosphate were added to the system at the end of each hydrometer test sequence, stirred, and allowed to soak for about 20 hours. The hydrometer procedure was followed and the phosphate addition repeated. The time required to attain maximum dispersion varied with the clay-water system and took as long as 3 weeks in the calcium-clay hard-water system. The possible effect of the time element on the validity of the results was recognized but the described procedure was adopted because of the space limitations of the laboratory and the time allotted to the study. The objection to this method was the possibility of the phosphate reverting to PO_4 ionization products of phosphoric acid an orthophosphate in the time elapsed during the experiment. However, some checks that were made using single optimum applications of phosphates to clay-water systems, showed no appreciable differences in the results. Also, the temperatures involved in the study were of such a range as to restrict reversion to a minimum. The latter statement agrees with published statements by phosphate manufacturers.

The method described above was followed during both years of the investigation. It proved expedient and allowed for a greater number of tests than would have been possible otherwise.

HYDROMETER ANALYSIS

The hydrometer test procedures used were patterned after standard wet mechanical analysis methods with modifications to adapt them to the objectives of this investigation (see the section "Discussion of the hydrometer method"). The procedure was as follows:

1. 10 grams of air-dry colloid was placed in each hydrometer cylinder.
2. Each cylinder was filled to the 1 liter mark with either distilled water or previously prepared synthetic water. The mixture was allowed to stand for 24 hours with occasional mixing.
3. A cylinder was filled with the same water as that used in the test, to act as a check on temperature and other effects.
4. The hydrometer was inserted into the check cylinder, and the reading recorded.
5. The samples were thoroughly mixed for a period of 1 minute by one of the following methods:
 - a. The hydrometer cylinder was covered with the palm of the hand and the suspension mixed by vigorous end-over-end shaking of the cylinder.
 - b. A mixing tool was inserted (a large rubber stopper fixed to the end of a glass rod) into the cylinder and moved rapidly up and down.
6. A clock or stopwatch was started as the mixing was stopped.
7. The hydrometer was carefully inserted into the suspension.
8. The percentage of clay in suspension was read and recorded 1 minute and 4 minutes after mixing.
9. The hydrometer was placed in the check cylinder and the observed reading recorded, thereby accounting for changes in temperature and electrolyte effects. This value was applied to the readings in the sample as a correction.
10. Additional readings were made on the sample and the check cylinder 19, 60, 435, and 1,545 minutes after mixing.
11. Specified amounts of deflocculent were added to the sample and to the check cylinder and steps 4 through 10 were repeated.

The hydrometer used was an ultrasensitive instrument that measures 10 grams of soil per liter at maximum reading. This instrument was used to enable work in the same range of concentration (about 1 percent) as was used in field experiments on sediment lining. When the salt concentration in the water was high and the amount of deflocculent was large, readings were beyond the range of the sensitive hydrometer and it was necessary to use a standard hydrometer calibrated to 60 grams of suspended material per liter.

RESULTS AND DISCUSSION

Many attempts have been made to devise a universal means of comparing the results from hydrometer tests and from other methods of mechanical analysis. Where large numbers of analyses were made, no rapid visual method of comparing the results was available. The primary deterrent was the lack of a suitable standard of comparison.

In the present investigation, interest centered on the relative efficiency of the various phosphate deflocculents. By adoption of one set of data as a standard of comparison, the relative dispersion characteristics of one clay in different phosphate-water systems could be evaluated. The numerical relation between the standard and the individual set of data is referred to as "the index of dispersion."

The data for sodium-saturated clays in distilled water with no deflocculent were selected as the standard of comparison for computation of dispersion indices.

Each sequence of tests on each clay type started with no deflocculent added. Because there was a sequence for each of three types of deflocculent using distilled water, this provided 3 runs on each clay that were duplicates, that is the same amount of clay dis-

persed in identical liquid media. This provided a usable standard with several advantages:

1. There were duplicate tests that could be averaged.
2. Sodium-saturated clays in distilled water represent near optimum dispersion.
3. The aqueous medium is salt free and does not introduce any extraneous electrolytic effects into the system.
4. The individual size distribution curves for a given clay were similar. Therefore the standard should be reproducible.

In the test procedure used, hydrometer readings were made 1, 4, 19, 60, 435, and 1,545 minutes after mixing the sample. As the grain-size distribution for all samples of a given type of clay was presumably the same, the sum of these readings would represent the relative dispersion of the sample. The average of the sum of the readings for 3 runs on each sodium-saturated clay in distilled water with no deflocculent was used as a standard or 100 percent dispersion. For Volclay, a montmorillonite-type clay, the average sum was 532; for kaolinite it was 453; and for illite it was 395. The dispersion indices were computed as in the following example.

For calcium-saturated Volclay in distilled water with 0.5 grams per liter of sodium tripolyphosphate added, the corrected hydrometer readings at the specified times were 90, 83, 69, 52, and 41 percent of dispersed weight. The total is 404 and the dispersion index is $404 \div 532 \times 100 = 75.9$ percent.

Thus each test run was compared on a percentage basis with the standard for the type of clay being tested.

The computation of dispersion indices requires that there be no missing data. The hydrometer readings in the standard at 1, 4, 19, 60, 435, and 1,545 minutes must be matched by readings at the same time intervals in the hydrometer run being studied. However, 1 or more of these readings were omitted during several tests, the reasons being time, expediency and apparent end to sequence. Examination of the data and the laboratory procedures used indicated that the missing readings lay within narrow definable limits and could be supplied with reasonable accuracy by extrapolation and interpolation. The following criteria were followed in substituting for missing data:

1. Missing values were assumed to be equal to or less than those preceding them in a series.
2. Incomplete curves were compared with complete size distribution curves in the same system and the missing data was chosen to make their curve shapes conform.
3. Notes on original data sheets such as references to clear surface breaks and floc formation, were used as guides in determining the extrapolated values.
4. Dispersion indices for a given system were plotted and any significant deviation from a norm was rechecked.

The results of the hydrometer analyses are presented in the section "Tables of Data and Dispersion Indices"

in tables 2 through 19 and are summarized for discussion in figures 1 to 11. Figures 1 to 11 are graphs of the dispersion indices versus the amount of deflocculent as listed in the tables of base data. The dispersion indices are plotted as ordinates with the abscissa of the point being the amount of deflocculent. Both are on linear scales as indicated. All graphs are labeled to indicate the colloid, type of water and ion saturation. The deflocculent used is indicated by the type of line in the individual graphs. The line coding used consistently through all of the summary curves is as follows:

Sodium tripolyphosphate —————
 Sodium hexametaphosphate — — — — —
 Sodium hexametaphosphate plus sodium carbonate — — — — —
 Sodium tetrapyrophosphate — — — — —

SODIUM MONTMORILLONITE IN DISTILLED WATER

Sodium montmorillonite was in a well-dispersed state when at equilibrium with distilled water (fig. 37A). This was in accord with dispersion theories (See section "Theory of clay-mineral behavior in dilute suspension", by R. F. Miller.) in that there is no electrolyte contribution from the water and the inherent negativity of the montmorillonite particles is at equilibrium with sodium, the least opposing cation to dispersion. The introduction of phosphate deflocculents into the system increased the index of dispersion beyond that of the standard. There was little difference among the three reagents in their effect on percentage of dispersion.

The improvement in dispersion of the system was probably due to sequestration of multivalent cations still present on the sodium saturated clay surfaces. The energy relations between ions and surfaces preclude the complete replacement by mass action of multivalent ions by sodium. Sequestration reduces this difficulty and increases the degree of sodium saturation. It is also possible, but less likely, that dispersion may have been improved by increasing the negativity of the montmorillonite particles by phosphate anion adsorption to clay edges.

CALCIUM MONTMORILLONITE IN DISTILLED WATER

The calcium montmorillonite was in a flocculent state when at equilibrium with the distilled water (fig. 37B). Unlike sodium saturation, calcium saturation may be completely effected by mass action. Thus, the exchange complex of the clay was probably 100 percent calcium and these closely held, divalent ions decreased the intensity of the clay negativity. The particles could then approach each other to the point where attractive forces become effective, thereby inducing floc formation and more rapid settling velocities.

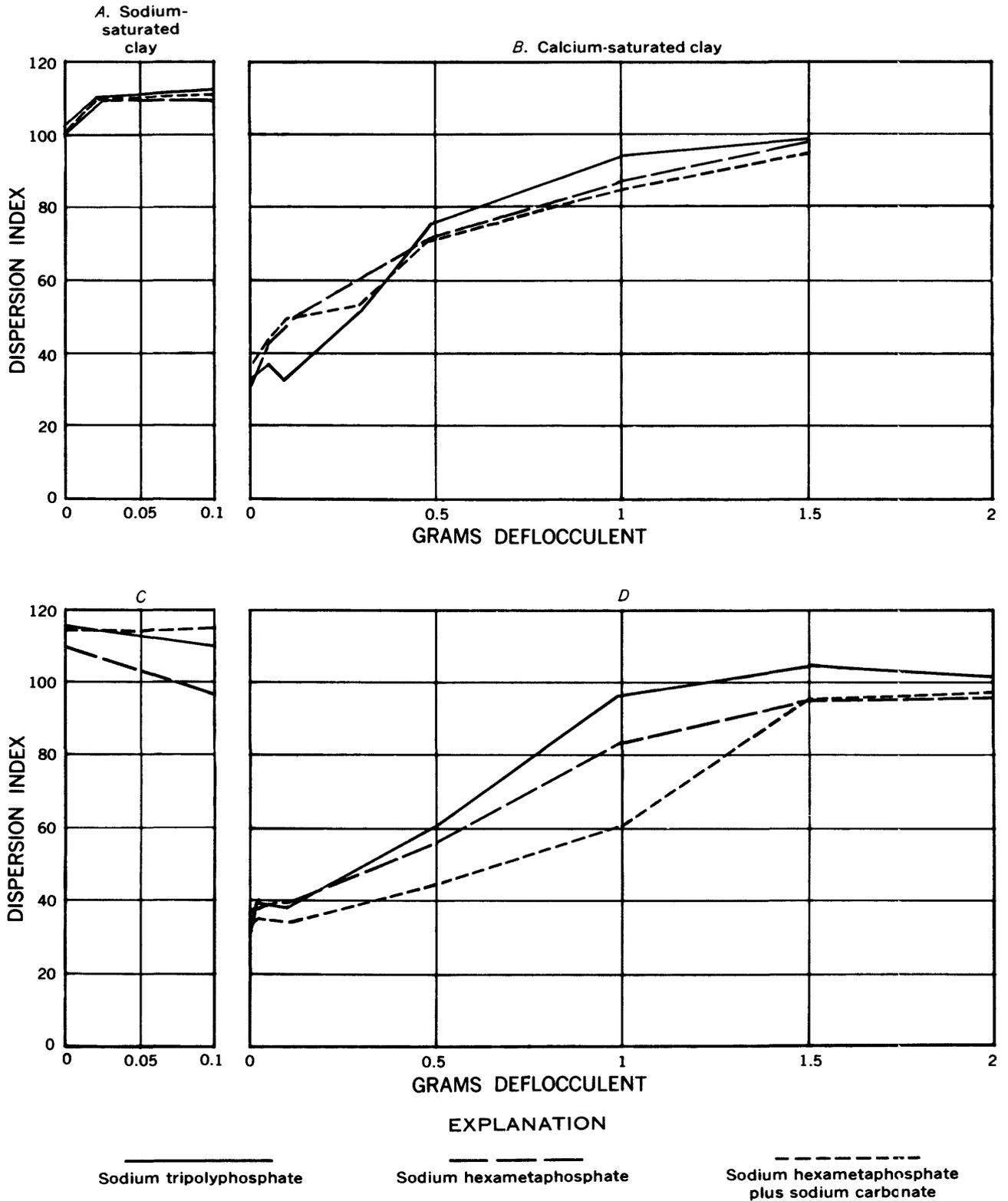


FIGURE 37.—Dispersion characteristics of sodium- and calcium-saturated montmorillonite in distilled and soft water. A, B, distilled water; C, D, soft water.

The introduction of phosphate deflocculents into this system improved dispersion. The slope of the index curve was greatest up to 70 percent; beyond this point there was a smaller increase in dispersion per unit weight of deflocculent. This point of maximum efficiency (70 percent) corresponds to 5 percent deflocculent per unit weight of clay.

At the 70 percent dispersion index there was little difference among the dispersants. Below this point, the reagents in the order of their efficiency in increasing the percentage of dispersion were: Sodium hexametaphosphate, sodium hexametaphosphate plus sodium carbonate, and sodium tripolyphosphate. Beyond the 70 percent dispersion index, sodium tripolyphosphate had a slight advantage over the other two.

The greater efficiency of sodium hexametaphosphate up to the 70 percent dispersion index was probably a function of its long chain polymer structure. Because the calcium montmorillonite-distilled-water system represented a high degree of neutralization of clay negativity, long chain hexametaphosphate polymeric anions could probably get closer to the clay edges than in other systems. Such contact may have facilitated the adsorption of these anions to the clay particle by contact with exposed positive charges (Al^{+++}) at these edges. This could improve dispersion by increasing the negative charge of the clay particles and by facilitating sequestration of the tightly bound Ca^{++} ions.

The apparent supremacy of sodium tripolyphosphate above the 70 percent index may be attributable to its greater supply of dissociated Na^+ . Displacement of Ca^{++} by Na^+ is by mass action and it may require more Na^+ in this range than can be supplied by the hexametaphosphate. Sequestration facilitates dispersion but a calcium-saturated system also requires mass action displacement by sodium.

SODIUM MONTMORILLONITE IN SOFT WATER

Sodium montmorillonite was in a semidispersed state when at equilibrium with soft water (fig. 37 *C*). The system seemed dispersed because of the turbidity throughout the hydrometer columns. However, a clear-water break soon developed at the surface (before a 24-hour period) and indicated that maximum dispersion had not been attained. Apparently, the ion concentration about each clay particle permissible for maximum dispersion had been exceeded and consolidation had taken place wherein porous flocs of material were compressed, leaving clear water at the surface.

The introduction of phosphate deflocculents into this system did not improve dispersion; in fact, the depth of clear-water breaks increased directly with the amount of deflocculent added. This was probably due to

electrolytic concentrations and compression of the diffuse cloud of cations about the clay particles. Sodium tripolyphosphate and the mixture of hexametaphosphate plus sodium carbonate was least detrimental to dispersion in this system.

CALCIUM MONTMORILLONITE IN SOFT WATER

The calcium montmorillonite was flocculated when at equilibrium with the soft water (fig. 37 *D*). This system showed properties similar to that of the calcium montmorillonite in distilled water. The high electrolyte content of the soft water apparently served to repress the dispersive tendency of the montmorillonite clay.

Introduction of phosphate deflocculents into this system improved dispersion. The phosphate dispersants ranked in efficiency in the order of possible displacement of calcium by sodium as follows: sodium tripolyphosphate, sodium hexametaphosphate, and sodium hexametaphosphate plus sodium carbonate. Sodium tripolyphosphate with the highest percent sodium per unit weight of salt was superior. This system contained hard (calcium) clays requiring mass-action displacement by sodium ions.

SODIUM MONTMORILLONITE IN HARD WATER

The sodium montmorillonite at equilibrium in hard water (fig. 38*A*) was in a semiflocculent state. The dispersion index at zero deflocculent was 80 and was accompanied by a clear-water break at the surface. This system could be better described as a high flocc. Calcium ions apparently displaced sodium from ion exchange surfaces, reducing the negativity of the montmorillonite particles and compressing the diffuse outer layer of associated cations.

The introduction of phosphate deflocculents into this system improved dispersion only slightly. This was probably due to the increase in electrolyte content from the added dispersant counteracting any possible benefit from replacing Ca^{++} ions with Na^+ ions.

CALCIUM MONTMORILLONITE IN HARD WATER

The calcium montmorillonite in hard water (fig. 38*B*) was in a flocculent state at equilibrium. Introduction of phosphate deflocculents improved dispersion up to a maximum at 30 percent deflocculent per weight of clay. Dispersant addition not only increased dispersion but caused the formation of a white precipitate. Analysis of the precipitate by X-ray diffraction and spectrography indicated that it was a complex of gypsum and phosphate.

The formation of this precipitate may be explained by review of the electrolyte content of the system. The

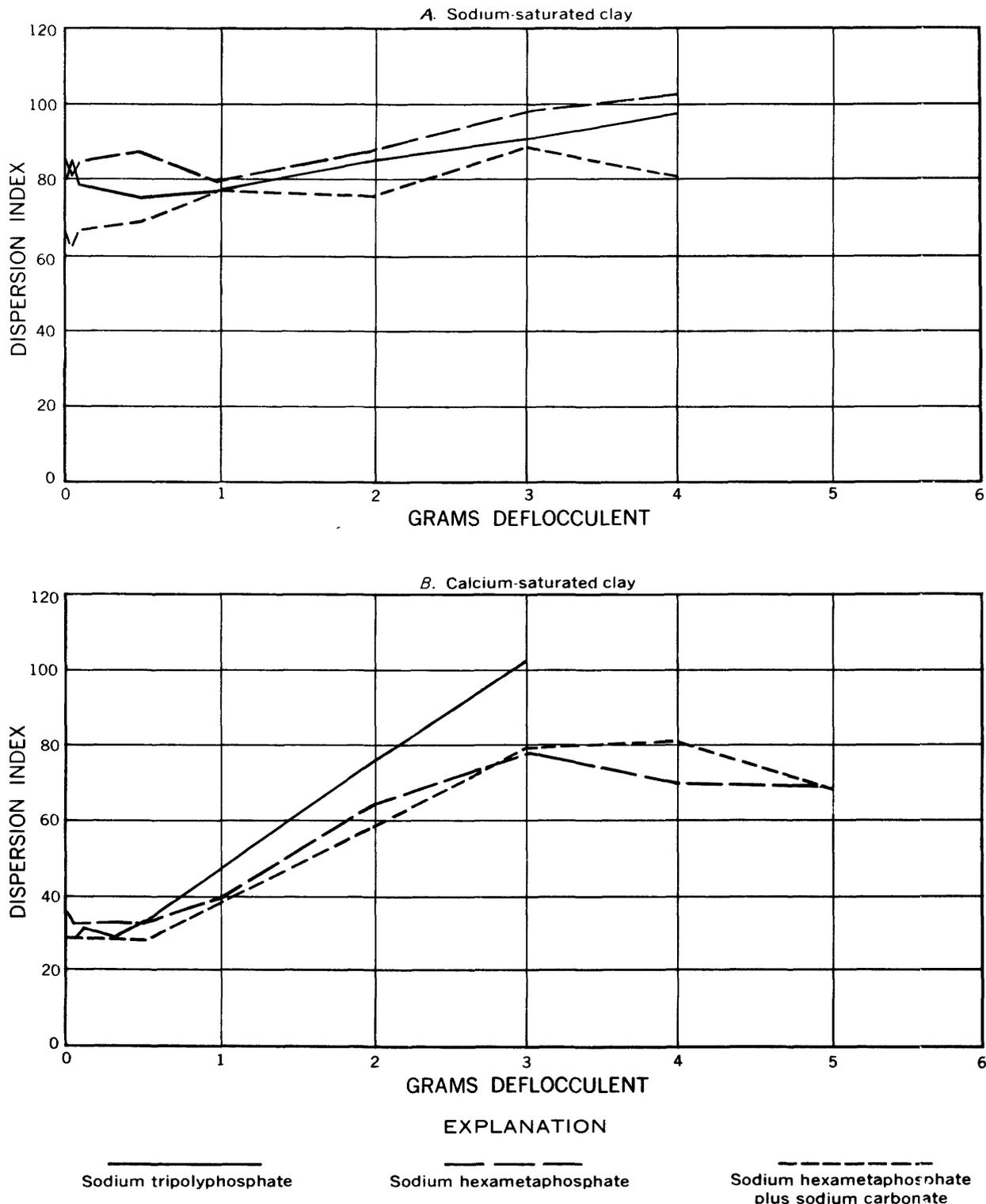


FIGURE 38.—Dispersion characteristics of sodium- and calcium-saturated montmorillonite in hard water.

anions of the calcium and magnesium salts in the hard water were sulfate (SO_4^-). The composition of the water was such that the solubility product of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was close to its limit. The addition of elec-

trolyte in the form of phosphate deflocculents possibly caused the system to exceed the solubility limit of the gypsum-phosphate complex, thereby causing it to precipitate. The complex may be the result of the affinity

of the phosphate polyanions for Ca^{++} ions causing them to be carried down with the calcium sulphate. The removal of Ca^{++} ions from the system by sequestration and precipitation apparently softened the water and improved the dispersion.

Sodium tripolyphosphate seemed most efficient, probably because of its greater content of dissociated sodium concurrent with its sequestering capacity. The dissociated sodium is needed to replace exchangeable calcium from the clay. Dehydrated sodium phosphates are poor sources of sodium for displacement of calcium from exchange surfaces by mass action.

SODIUM KAOLINITE IN DISTILLED WATER

Sodium kaolinite was dispersed when at equilibrium with distilled water (fig. 39A). The addition of phosphate deflocculents improved dispersion probably by sequestering any stray multivalent cations still in the system and by increasing clay negativity through sorption onto clay edges.

CALCIUM KAOLINITE IN DISTILLED WATER

Calcium kaolinite was flocculated when at equilibrium with distilled water (fig. 39B). The phosphate de-

flocculents improved dispersion in the following order: Sodium hexametaphosphate, then sodium carbonate plus sodium hexametaphosphate, and last, sodium tripolyphosphate. The superiority of the sodium hexametaphosphate treatments indicates that increased negativity from adsorption of polyanions helped increase the dispersability of kaolinite in this system above the dispersion attainable from Ca^{++} ion sequestration alone

SODIUM KAOLINITE IN SOFT WATER

Sodium kaolinite was partly flocculated when at equilibrium with soft water (fig. 40A). This was probably due to the effect of the high salt content and the 5 milliequivalents per liter of Ca^{++} plus Mg^{++} in the soft water. Addition of phosphate deflocculents to the system increased dispersion. The order of efficiency of the three reagents was: Sodium hexametaphosphate plus sodium carbonate, sodium tripolyphosphate, and last, sodium hexametaphosphate. The fact that the degree of dispersion was greater in the two alkaline systems indicates that dissociation of OH^- ion from alumina sheets increased the negativity of clay particles. The superiority of sodium hexametaphosphate buffered by

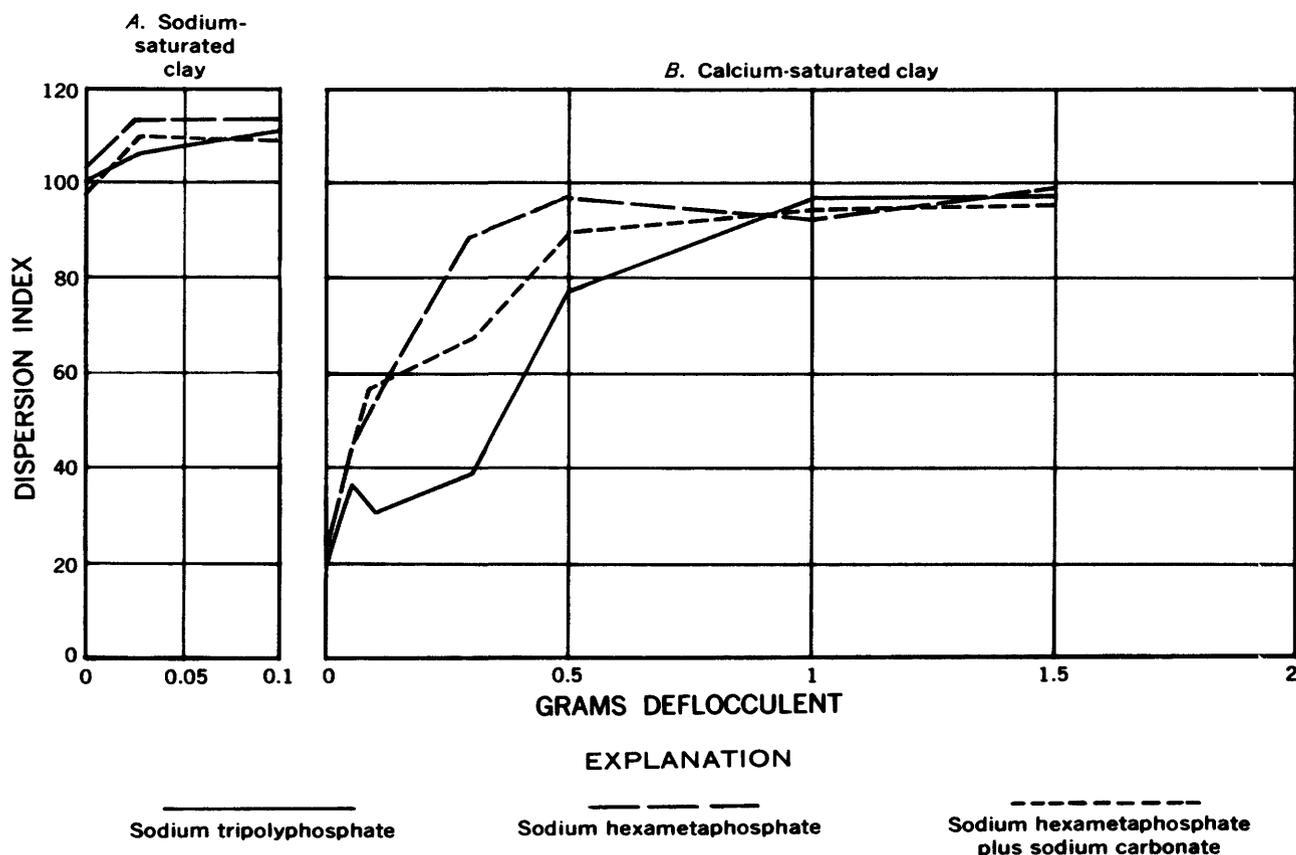


FIGURE 39.—Dispersion characteristics of sodium- and calcium-saturated kaolinite in distilled water.

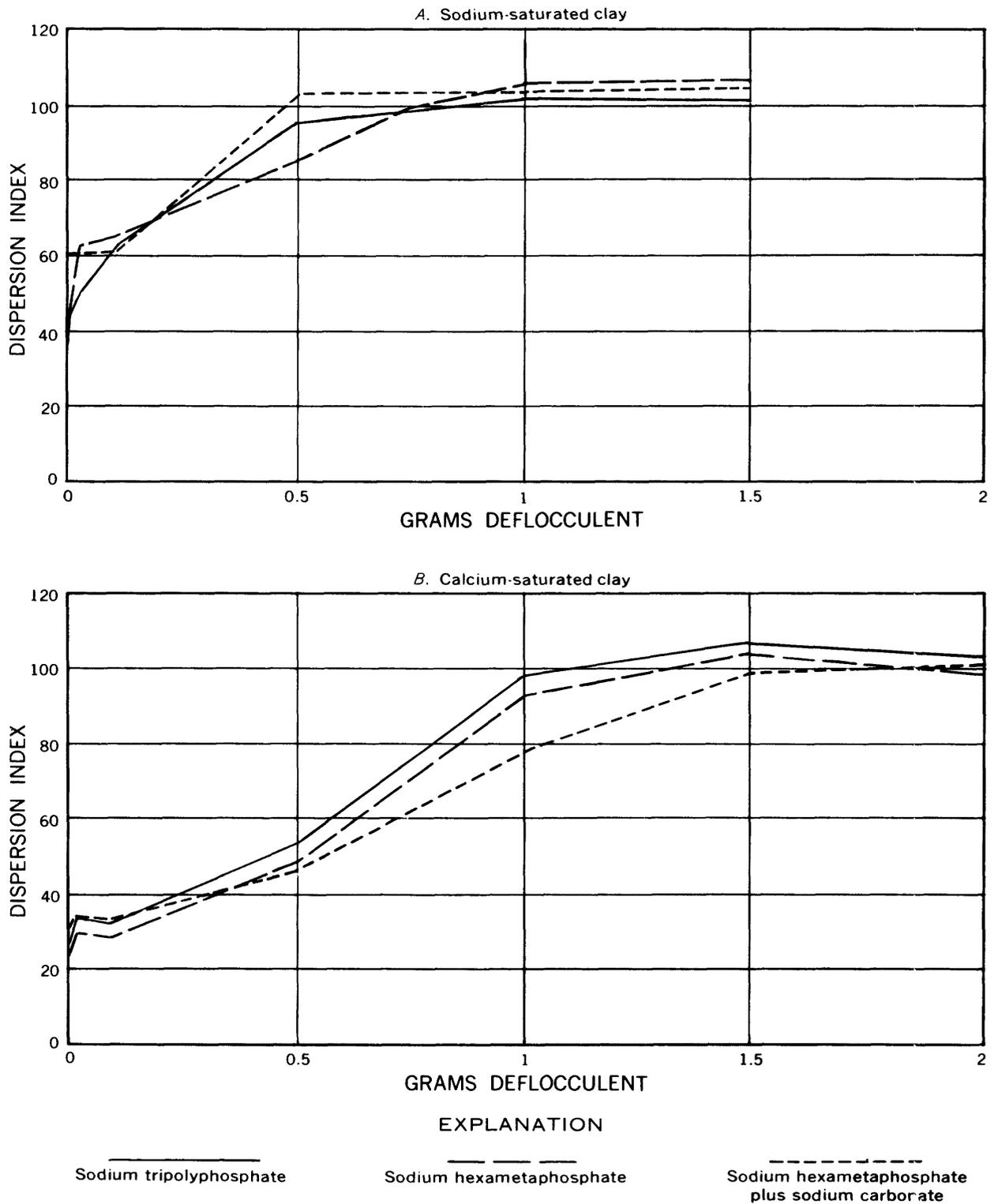


FIGURE 40.—Dispersion characteristics of sodium- and calcium saturated kaolinite in soft water.

sodium carbonate indicates that increased negativity from adsorption of polyanions also was effective in dispersing the system.

CALCIUM KAOLINITE IN SOFT WATER

Calcium kaolinite was flocculated when at equilibrium with soft water (fig. 40B). Phosphate deflocculents increased dispersion in the following order: Sodium tripolyphosphate, sodium hexametaphosphate, and sodium hexametaphosphate plus sodium carbonate. The reaction order indicates that sequestration of Ca^{++} ions and replacement of these ions with monovalent Na^+ ions was effective in dispersing this system.

SODIUM KAOLINITE IN HARD WATER

Sodium kaolinite was flocculated when at equilibrium with hard water (fig. 41A). The introduction of phosphate deflocculents into the system caused a gradual increase in degree of dispersion. The increase in dispersion was coincident with formation of a precipitate similar to that formed in montmorillonite-hard-water system, that is, a complex of gypsum and phosphate.

There was little difference between the reagents with respect to dispersion efficiency. The sodium tripolyphosphate, however, produced a slightly higher index than the other two, reflecting its greater capacity for sequestering Ca^{++} ions. The high electrolyte content of this system apparently prevented it from attaining as high a degree of dispersion as existed in the standard sodium kaolinite distilled water system.

CALCIUM KAOLINITE IN HARD WATER

Calcium kaolinite was flocculated when at equilibrium with hard water (fig. 41B). Both clays and water were dominated by the calcium ion and the environment was especially conducive to flocculation.

The introduction of phosphate deflocculents improved dispersion coincident with the formation of a gypsum-phosphate precipitate. Sodium tripolyphosphate was most efficient, followed by the sodium hexametaphosphate-sodium carbonate mixture with sodium hexametaphosphate last. The superiority of the two alkaline buffered dispersants over acid sodium hexametaphosphate indicates that the negativity of kaolinite may have been increased in the alkaline systems by dissociation of OH^- ions in the alumina sheet.

SODIUM ILLITE IN DISTILLED WATER

Sodium illite was dispersed when at equilibrium with distilled water (fig. 42A). The colloidal yield of the dispersed standard was only 25 percent, that is, only

one-fourth of the mass had a diameter of less than one micron.

The introduction of phosphate deflocculents into the system increased dispersion. This was probably due to sequestration of any stray multivalent ions still present. There was little or no difference in efficiency between the phosphates.

CALCIUM ILLITE IN DISTILLED WATER

Calcium illite was flocculated when at equilibrium with distilled water (fig. 42B). Phosphate deflocculents did not improve dispersion in this system.

SODIUM ILLITE IN SOFT WATER

Sodium illite had a dispersion index of a little more than 60 percent when at equilibrium with soft water (fig. 43A). This decrease of dispersion in distilled water must be attributed to the high salt content of the soft water and the effect of the divalent ions, Ca^{++} and Mg^{++} , in the water.

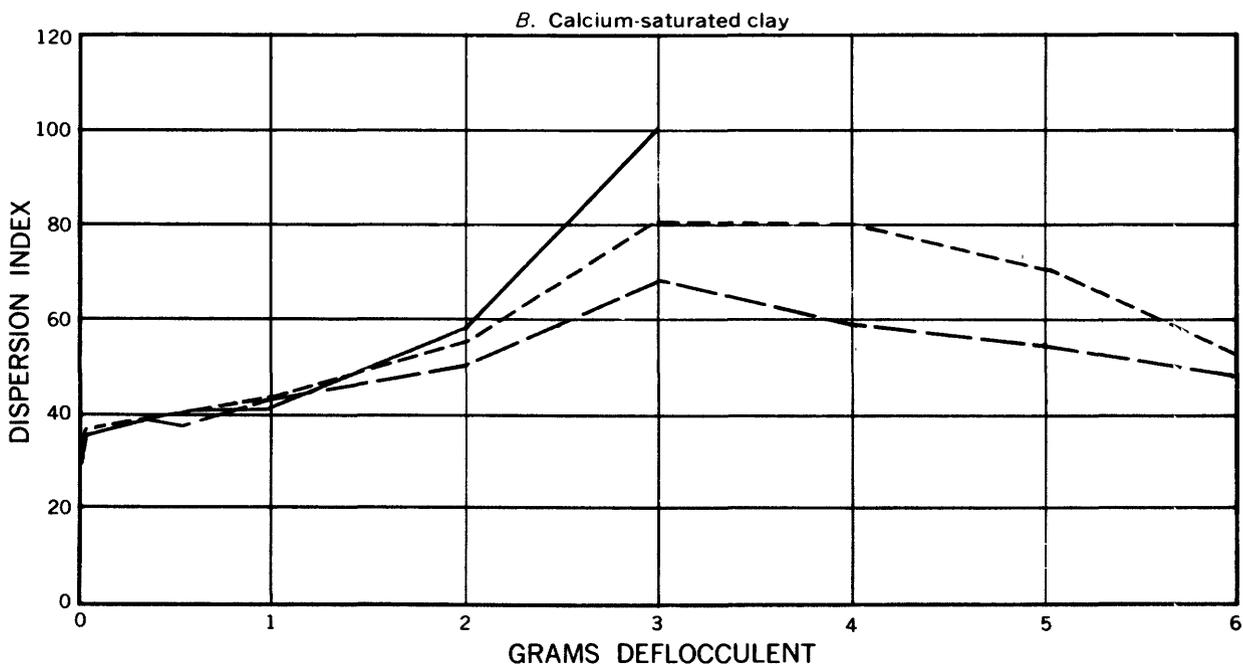
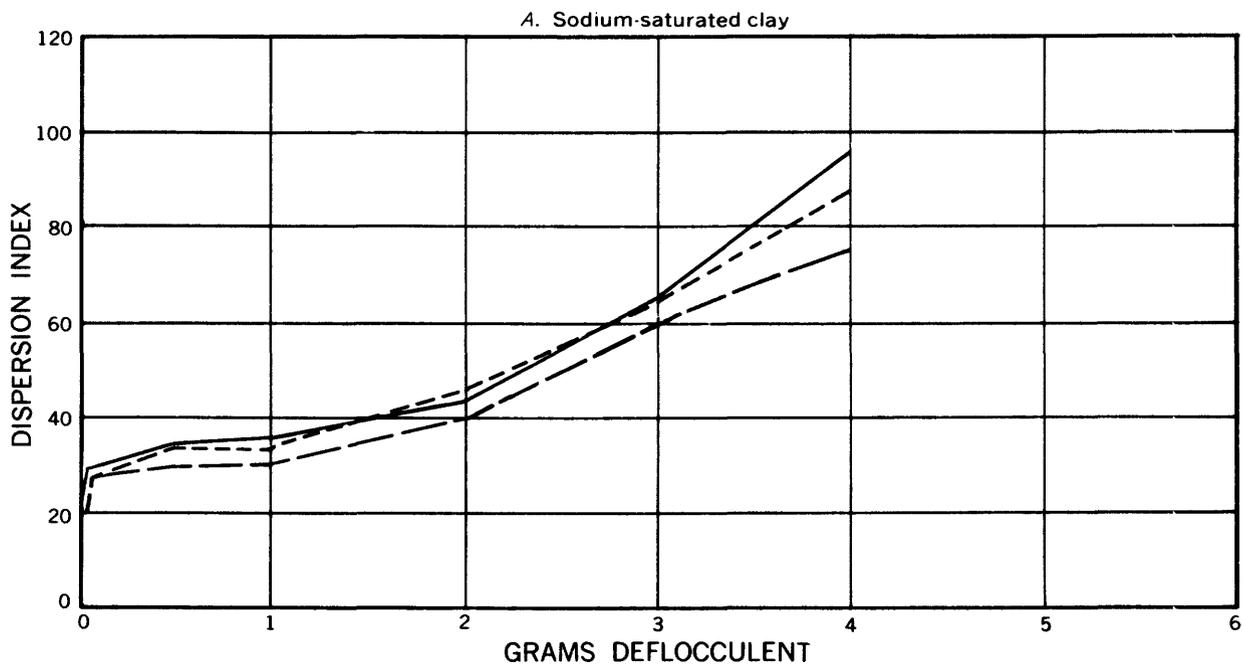
The introduction of phosphate deflocculents into the system produced an increase in degree of dispersion. Only treatments containing long chain polymers (hexametaphosphates) progressively improved dispersion, indicating benefits from increased negativity from adsorption of long chain polyanions to clay surfaces. The ineffectiveness of sodium tripolyphosphate indicates little benefit to the system by the sequestration mechanism. The increase in dispersion efficiency of sodium tripolyphosphate, after this chemical became more concentrated in the system, cannot be explained on the basis of available data.

CALCIUM ILLITE IN SOFT WATER

The calcium illite was in a flocculent condition when at equilibrium with soft water (fig. 43B). The addition of phosphate reagents did not materially increase the dispersion of the system. This indicates that it is impractical to improve the dispersibility of a calcium-saturated clay by the use of sequestering agents. The relative efficiencies of the deflocculents in this system were the same as those observed when sodium-saturated illite was studied in the soft water. The similarity between curves in both systems indicates the same factors were effective with both the sodium- and calcium-saturated clays in the soft water.

SODIUM ILLITE IN HARD WATER

Sodium illite in hard water (fig. 44A) was flocculent and showed a dispersion index of slightly more than 40 percent when at equilibrium with hard water. This system exhibited dispersion characteristics similar to those of the sodium illite in soft water, indicating the



EXPLANATION

Sodium tripolyphosphate	Sodium hexametaphosphate	Sodium hexametaphosphate plus sodium carbonate

FIGURE 41.—Dispersion characteristics of sodium- and calcium-saturated kaolinite in hard water.

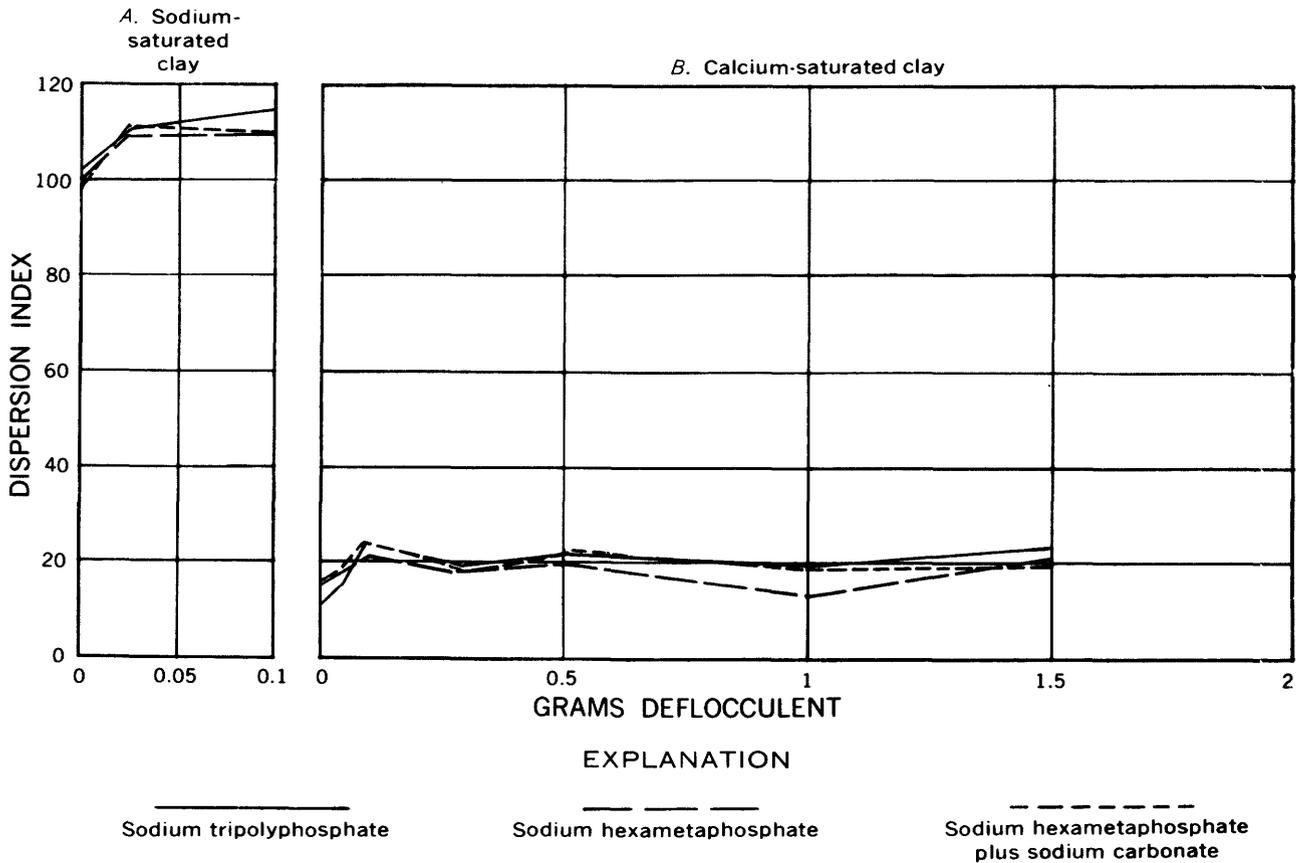


FIGURE 42.—Dispersion characteristics of sodium- and calcium-saturated illite in distilled water.

prevalance of similar factors in both systems. Apparently, long chain polymers were most effective in dispersing the system. The initial depression of dispersion in the sodium tripolyphosphate system could be related to an increase in the salt concentration without benefit from polyanion adsorption.

CALCIUM ILLITE IN HARD WATER

Calcium illite at equilibrium with hard water (fig. 44B) was flocculated. The increase in dispersion index through use of phosphate reagents was small, from about 20 percent to between 40 and 50 percent. Large quantities of the dispersants had to be added before dispersion was improved. The superiority of sodium tripolyphosphate at this point indicates that availability of Na^+ ions for displacement of Ca^{++} ions and ability to sequester Ca^{++} ions were most effective in improving dispersion. The data further indicate that it is impractical to attempt to disperse a calcium-saturated system with phosphate dispersants.

The illite and kaolinite used in the following phases of the study were treated to simulate ion saturation on a Wyoming bentonite sold by American Colloid Co. as Volclay. Circular 202 of this company indicates

that the relative sodium and calcium plus magnesium percentages in Volclay are 78.8 and 21.2 respectively. The dispersion characteristics of the above-treated clays were examined in distilled water and in a synthetic water of medium hardness, based on a prototype water from the Tri-County Canal system in central Nebraska. This water contained 6.2, 3.6, and 6.3 milliequivalents per liter respectively of calcium, magnesium, and sodium.

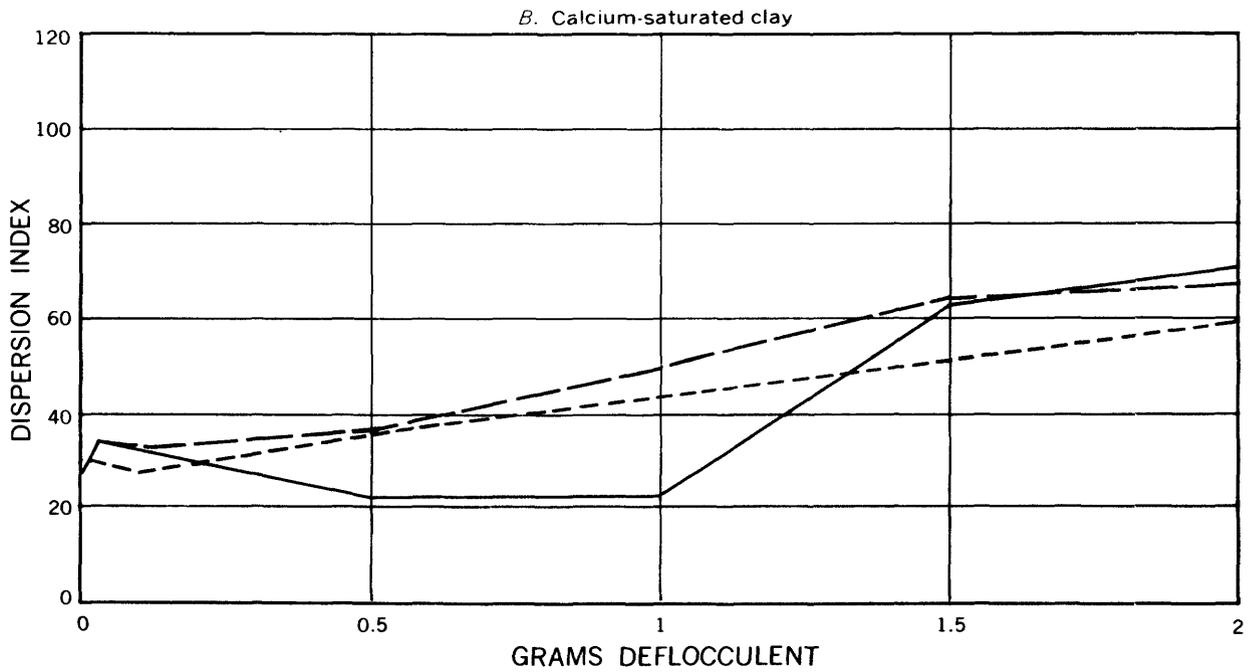
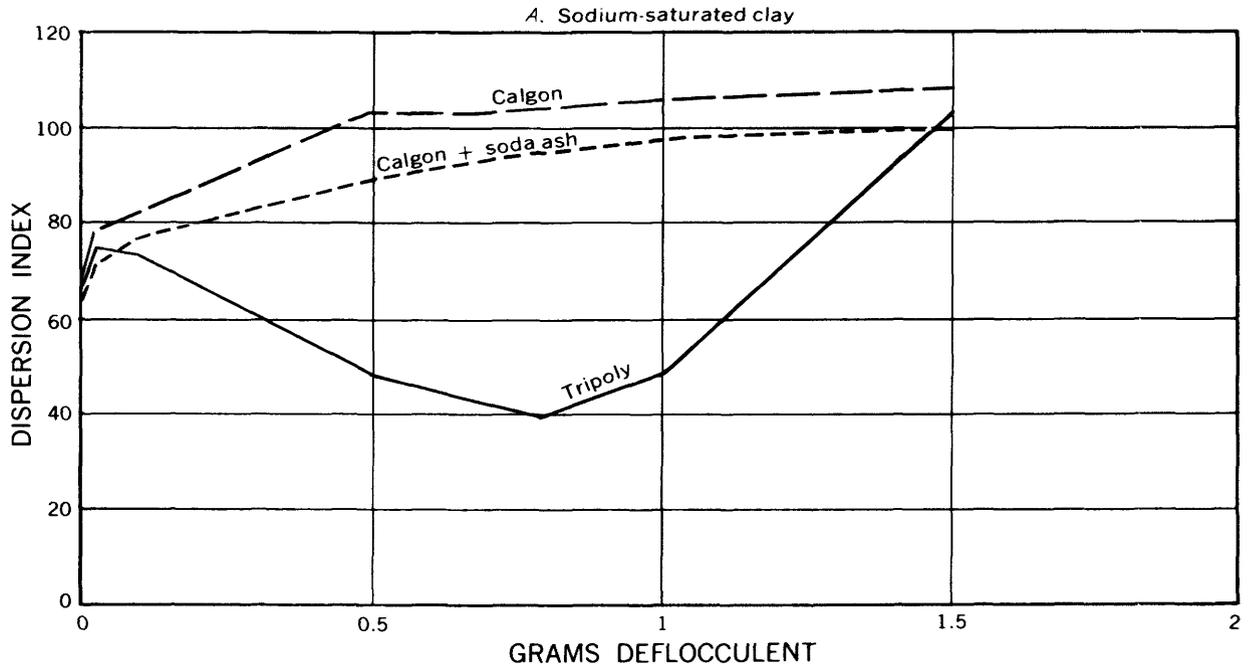
VOLCLAY IN DISTILLED WATER

Volclay was dispersed when at equilibrium with distilled water (fig. 45A). Not only was the water relatively free from cations but the exchangeable cations were in such proportion as not to effectively reduce the negativity of the montmorillonite particles.

The addition of phosphate deflocculents did not improve dispersion. The increase in electrolyte content probably counteracted any possible benefit by sequestration or polyanion adsorption.

VOLCLAY IN MEDIUM-HARD WATER

The dispersion index of the native montmorillonite medium hard water system (fig. 45B) was about 75 per-



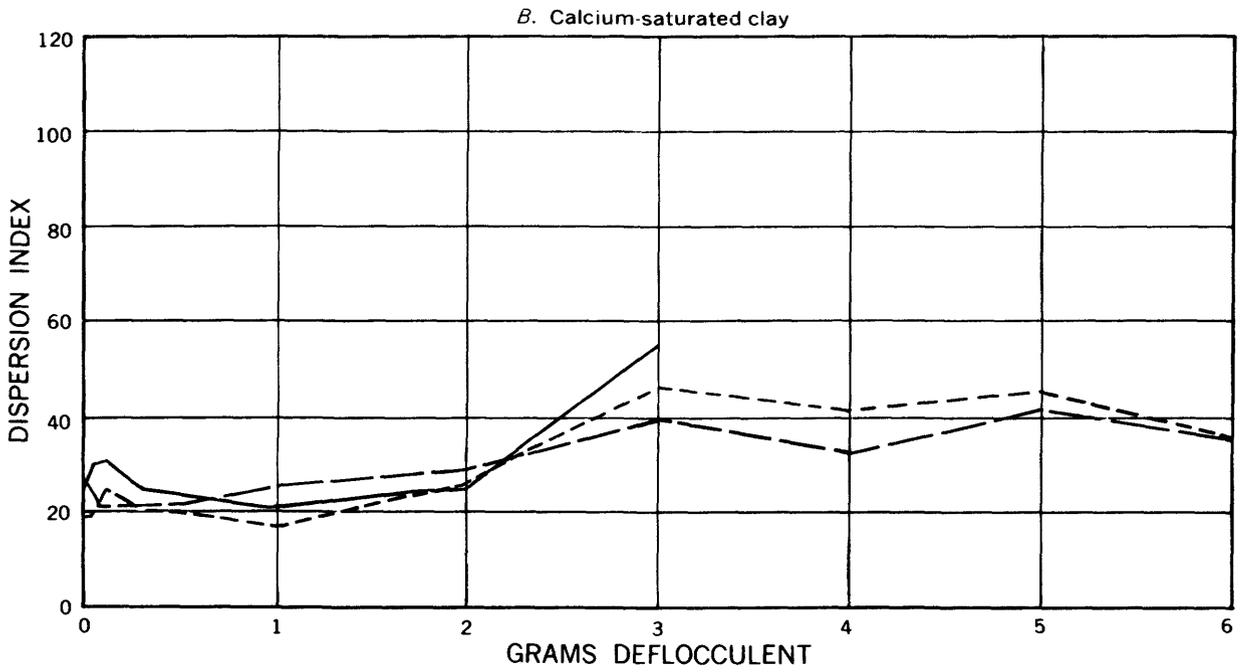
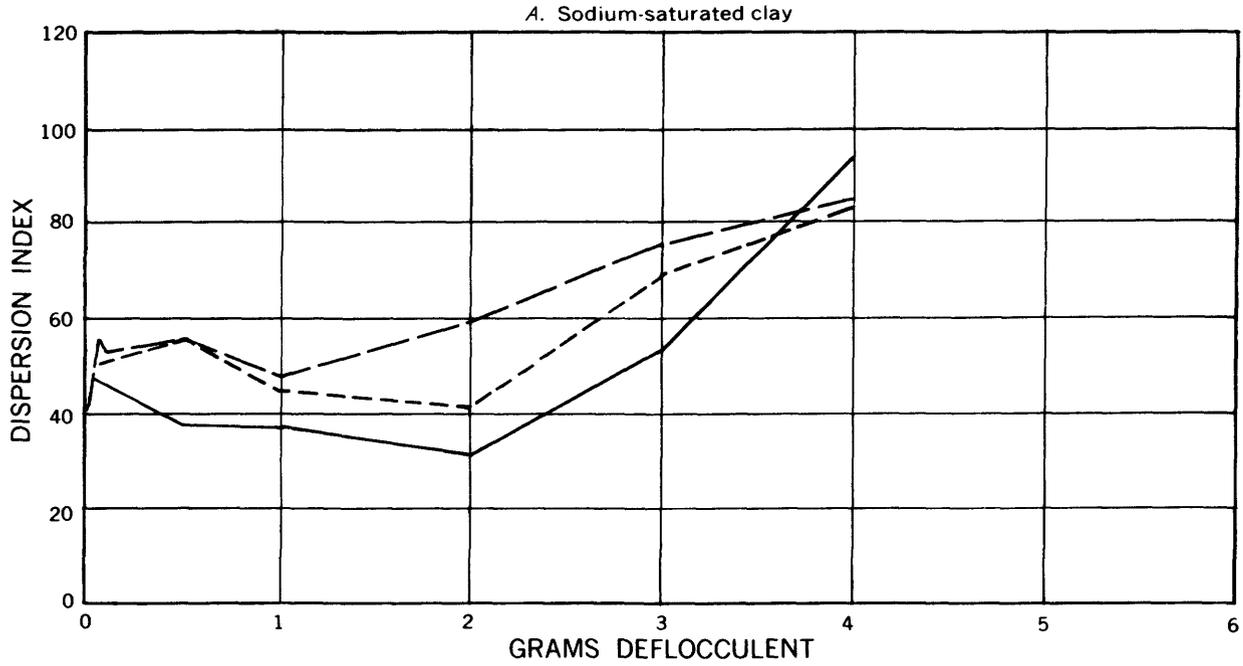
EXPLANATION

————— Sodium tripolyphosphate

----- Sodium hexametaphosphate

----- Sodium hexametaphosphate plus sodium carbonate

FIGURE 43.—Dispersion characteristics of sodium- and calcium-saturated illite in soft water.



EXPLANATION

Sodium tripolyphosphate
 Sodium hexametaphosphate
 Sodium hexametaphosphate plus sodium carbonate

FIGURE 44.—Dispersion characteristics of sodium- and calcium-saturated illite in hard water.

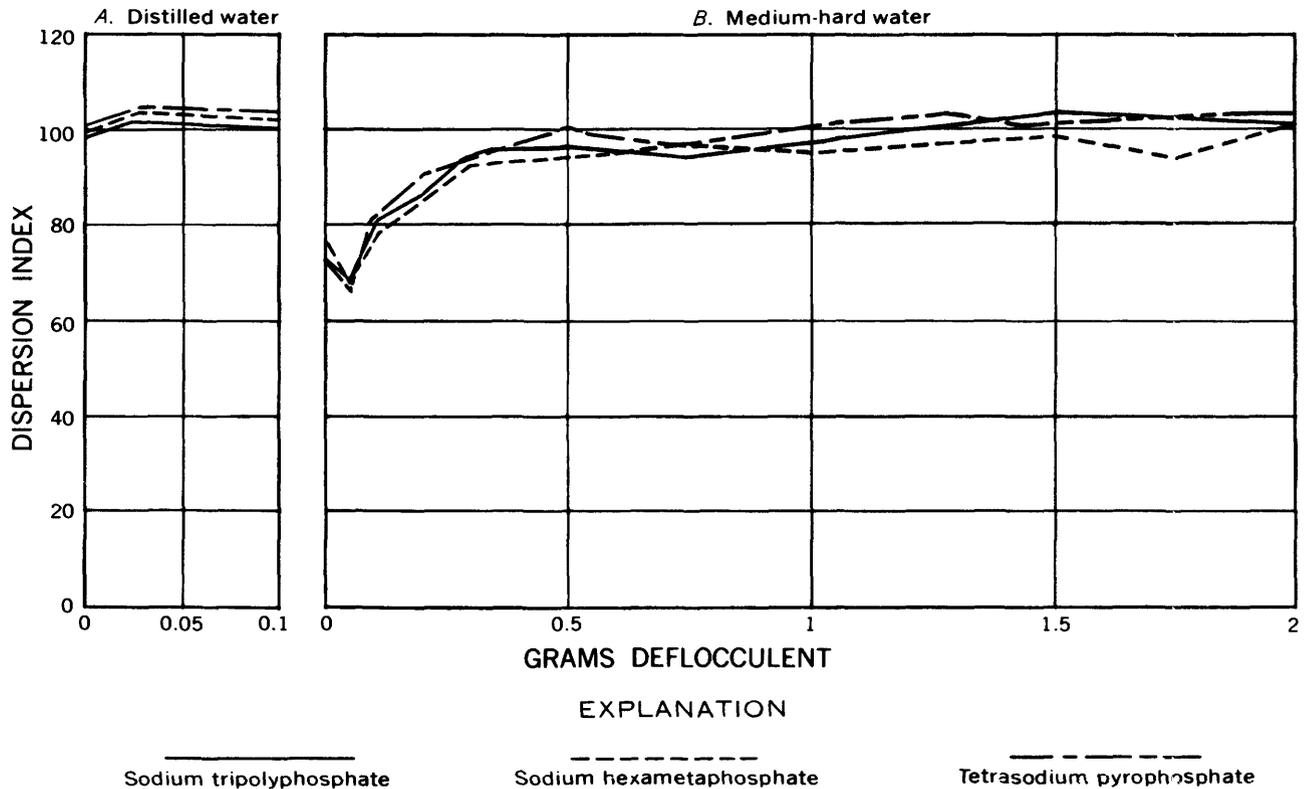


FIGURE 45.—Dispersion characteristics of Volclay in distilled and medium-hard water.

cent when at equilibrium. This was probably due to the flocculating effect of the divalent cations and the salt content of the water.

The introduction of phosphate deflocculents into the system improved dispersion. This may be attributed to displacement of multivalent ions by monovalent Na^+ ions, and sequestration of the multivalent ions. There was little difference between the deflocculents with respect to dispersion efficiency; but the dispersants did rank in the order of their sodium composition per unit weight, as follows: 1. tetrasodium pyrophosphate, 2. sodium tripolyphosphate, 3. hexametaphosphate.

KAOLINITE (78.8 PERCENT SODIUM SATURATED) IN DISTILLED WATER

This kaolinite was dispersed when at equilibrium with distilled water (fig. 46A). Again the environment was conducive to dispersion.

The introduction of phosphate deflocculents into the system did little to increase dispersion. The slight increase may be attributed to sequestration of divalent cations and possibly polyanion adsorption to clay edges. The latter possibility is remote because physicochemical consideration of the system indicate that the phosphate anions would have some difficulty in approaching the clay particles when the latter were surrounded by diffuse clouds of Na^+ ions; the more diffuse the clouds of ions

about the particles the more difficult the approach of negative ions to the clay surface.

KAOLINITE (78.8 PERCENT SODIUM SATURATED) IN MEDIUM-HARD WATER

The dispersion index of this system (fig. 46B) was 40 percent when at equilibrium. The electrolyte and divalent cation content of the water was sufficient to partly flocculate the system.

The introduction of phosphate deflocculents into the system improved dispersion. The partly flocculated system apparently allowed the approach of polyanions to the clay surfaces. This hypothesis is supported by the order of efficiency of the reagents, namely, sodium hexametaphosphate, sodium tripolyphosphate, tetrasodium pyrophosphate. The above order is that of decreasing length of polymer chain, which characteristic is related to efficiency in dispersing kaolinite through increasing the negativity of the clay by adsorption of polyanions to exposed edges.

ILLITE (78.8 PERCENT SODIUM SATURATED) IN DISTILLED WATER

The illite was dispersed when at equilibrium with distilled water (fig. 47A). However, it must be remembered that only 30 percent of the material was less than 1 micron in diameter when fully dispersed.

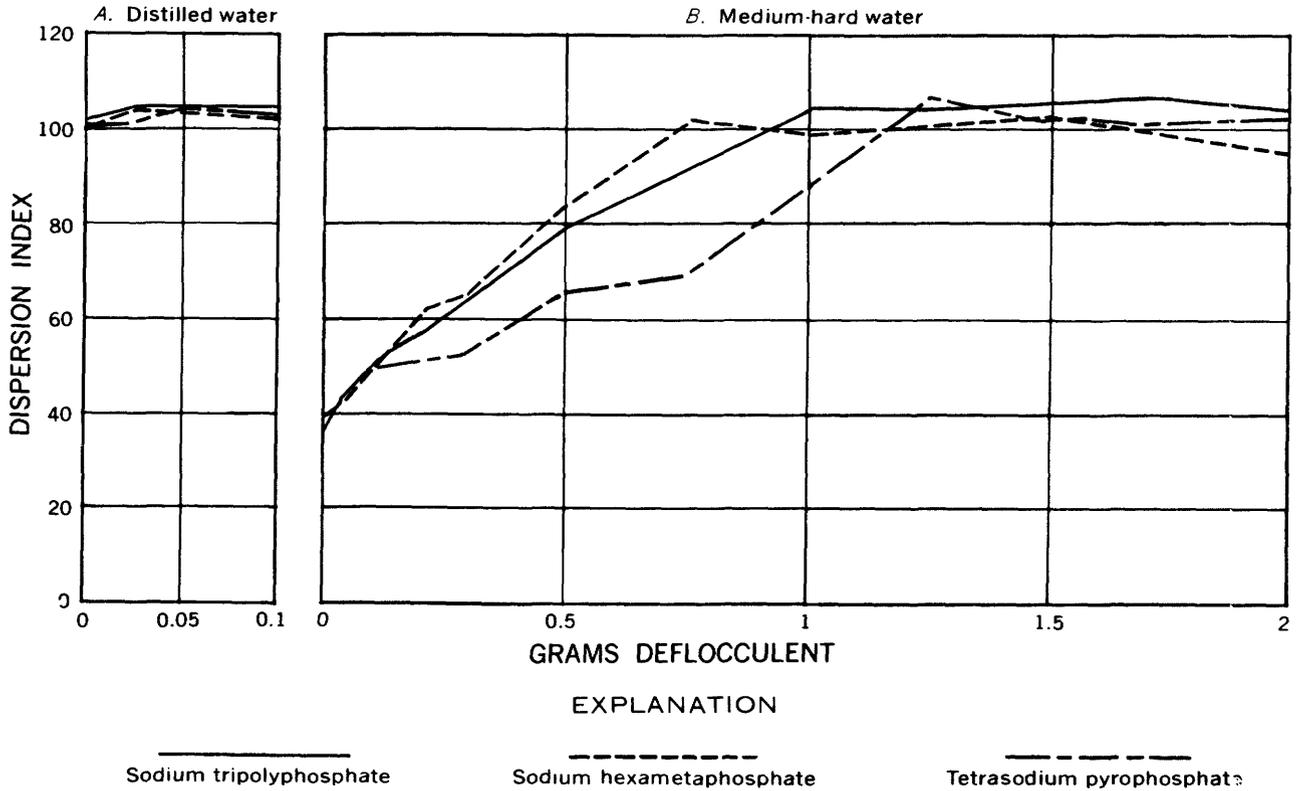


FIGURE 46.—Dispersion characteristics of kaolinite (78.8 percent sodium saturated) in distilled and medium-hard water.

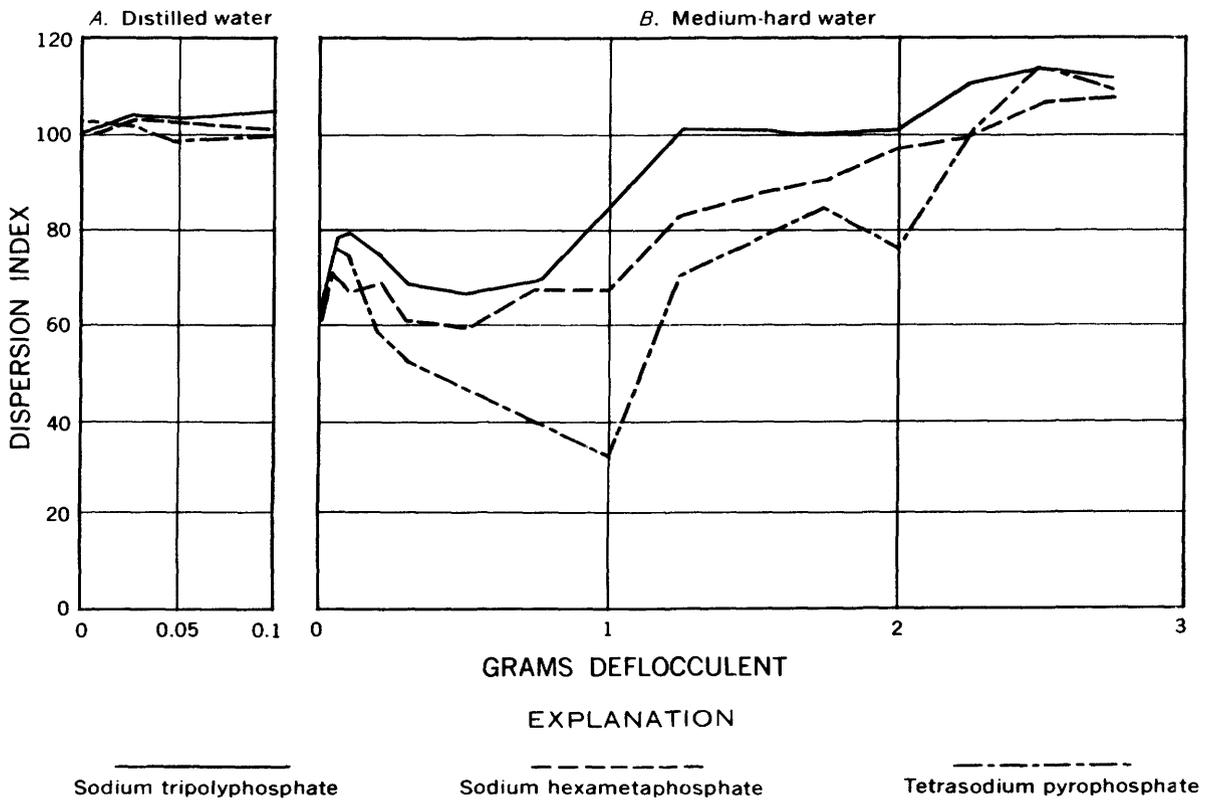


FIGURE 47.—Dispersion characteristics of illite (78.8 percent sodium saturated) in distilled and medium-hard water.

The addition of phosphate deflocculents into the system did not materially increase the dispersion. There was no marked difference among the reagents with respect to dispersion efficiency.

ILLITE (78.8 PERCENT SODIUM SATURATED) IN MEDIUM-HARD WATER

The illite was flocculated when at equilibrium with medium-hard water (fig. 47*B*). The data indicate that the degree of flocculation was not as great as in the calcium-illite hard-water system.

The addition of phosphate deflocculents into the system increased dispersion. Sodium tripolyphosphate was better than sodium hexametaphosphate and tetrasodium pyrophosphate was the least efficient. The order of the dispersants probably reflects the relative efficiency of the dispersants as sequestering agents. Tetrasodium pyrophosphate was superior only in systems where sodium was needed to displace Ca^{++} ions from exchange surfaces, which was apparently not needed in this system.

SUMMARY OF CONCLUSIONS

1. It is not practical to attempt to disperse calcium-saturated clays with hexametaphosphate, tripolyphosphate, or tetrasodium pyrophosphate.
2. Only clays that are easily dispersed in distilled water without the use of deflocculents should be used for sediment lining of canals if control of dispersion is a requirement.
3. Hexametaphosphate, tripolyphosphate, and tetrasodium pyrophosphate can control the degree to which clay particles are dispersed in waters varying in hardness (calcium and magnesium content) if the total salt content is not excessive.
4. The mechanism whereby the phosphate deflocculents disperse clay suspensions is probably a function of either divalent ion sequestration or increasing the negative charge of clay particles by adsorption of poly-anions, or both.
5. Montmorillonite clays are apparently the best source of colloidal particles for sediment lining of canals if control of dispersion and penetration of small voids are required.
6. Tripolyphosphate was the most efficient dispersing agent for control of montmorillonite dispersion in waters of low to medium hardness.
7. Sodium hexametaphosphate was generally superior for dispersion of kaolinite. The kaolinite tested was, however, easily dispersed by all the phosphate dispersants tested.
8. Illite was difficult to disperse and keep in suspension. When sodium saturated, however, it formed

a sticky paste, which may make it useful for filling cracks and large voids.

9. If the electrolyte (salt) content of the canal water is too high it may prevent the dispersion of clays even with the use of phosphate dispersants.

10. The point of complete sequestration of calcium and magnesium by phosphate dispersants was measured by using dye indicators normally used for calcium and magnesium determinations. However, the quantities of sequestering agent required for practical dispersion of clay in canal waters seldom coincided with total sequestration. The only practical method found for determining the quantity of sequestering agent required is to add different quantities to samples of fresh water and measure dispersion with a hydrometer. Fresh water is specified because the chemical composition of a stream varies with time, or calcium may precipitate out as calcium carbonate as the water becomes stagnant and cause an underestimation of the quantity of sequestering agent needed. The effects of organic matter dissolved in the water would also express itself and could be compensated for.

PROPERTIES OF CLAY MINERALS

By B. N. ROLFE

This section of the report discusses the clay minerals used in the investigation. It is not intended as a primer on clay mineralogy but as background material for a better understanding of the experimental data. The reader is referred to Grim (1953) for a more detailed treatment of the subject. A discussion of the behavior of clay minerals in suspensions is presented in the section "Theory of Clay Mineral Behavior in Dilute Suspensions" by R. F. Miller.

As the present study was designed to investigate basic dispersion characteristics of colloidal clays, it seemed expedient to simplify the problem by restricting the study to monomineralic clays. Therefore, three representative clay minerals were selected for the investigation of the dispersion characteristics of possible sedimenting materials.

Clay minerals are usually classified on the basis of structure and composition. Structurally, two units are included in the atomic lattices of most clay minerals. One unit is comprised of two sheets of closely packed oxygen or hydroxyl ions between which aluminum and, less frequently, magnesium or iron atoms are embedded in octahedral coordination, that is, each metallic atom is equidistant from six oxygen or hydroxyl ions. This arrangement of sheets will hereinafter be referred to as the octahedral unit.

The second unit is built of silica tetrahedrons in which a silicon atom is equidistant from four oxygen or hydroxyl ions. The silicon atoms apparently lie in a plane and form a hexagonal network. This sheet arrangement will be hereinafter referred to as the tetrahedral unit.

These two units form the building blocks for the formation of clay minerals. Classification is based on the arrangement of these units and on deviations from modal atomic composition. The three main types of clay minerals will be discussed, in relation to the clay materials used during the investigation.

KAOLINITE

Kaolinite is the most prominent member of the kaolin group of clays among which are kaolinite, dickite, nacrite and halloysite. Clays in this group are called 1:1 layer minerals because unit cells are composed of one tetrahedral unit joined to one octahedral unit. There is little or no atomic substitution in the units, and kaolinite may be regarded as consisting of model sheet units of silica tetrahedra and alumina octahedra. Because of the dimensional similarity between structural units along the *a* and *b* crystallographic axes, unit cells of octahedra and tetrahedra are readily formed and are fairly stable.

Substitution of one ion for another, called isomorphous substitution in clay mineralogy, is rare in the kaolinite minerals and the kaolinite clays are generally electrostatically neutral. Charge deficiencies at the broken edges of the *a* and *b* planes are both negative and positive. Anionic deficiencies along these broken edges are the probable sources of anion attraction and probably are the point of phosphate ion adsorption as is explained later. Slight irregularities in the cation composition of kaolinite, as well as cationic deficiencies at broken edges, may be sources of positive charge deficiencies. The cation exchange capacity of kaolinite minerals generally ranges from 3 to 15 milliequivalents per 100 grams of kaolinite material.

Kaolinite minerals generally occur in the upper size diameters of clays. They may be found as discrete particles with diameters as large as 20 microns but the median diameter is generally about 1 micron. The specific dispersion characteristics of kaolinite are discussed on page 254 but deflocculation is probably effected by increasing clay negativity via anion sorption of complex polyphosphates along the broken edges.

MONTMORILLONITE

Montmorillonite is the dominant member of the montmorillonite group of clay minerals, among which are montmorillonite, beidellite, hectorite, saponite

and nontronite. The clay used in the present study is commonly called bentonite and occurs abundantly in some parts of Western United States. The high-swelling bentonite, produced extensively in Wyoming, is usually composed mostly of sodium montmorillonite together with traces of cristobalite and volcanic ash, and it has the ability to absorb large quantities of water.

The montmorillonite group of clay minerals is classified as 2:1 layer minerals—the unit cells are composed of two tetrahedral units enclosing a single octahedral unit. Isomorphous substitution is common to both units. This substitution phenomenon results in an imbalance of charge within the montmorillonite lattice and is characteristic of the mineral. Substitution in either unit may be partly compensated by substitution in the other unit. However, substitutions in the montmorillonite lattice yield a net negative charge on the lattice. This negative charge is balanced by exchangeable cations, such as Ca^{++} or Na^+ , adsorbed between the layers and around their edges.

Discrete montmorillonite particles grow by continuous extension along the *a* and *b* axes and by stacking in the *c* direction. Bonding between unit cells is weak by comparison with kaolinite and is the reason for the small size of discrete montmorillonite particles, generally under 0.5 micron in diameter. Only cation exchange is assumed to take place on the planar surfaces of the montmorillonite particles whereas both cation and anion exchange occur at the edges. The probable ratio of planar to edge surfaces may be indicated by cation-anion exchange capacity ratios of 6.7 to 1.0. A similar comparison for kaolinite shows a ratio of 0.5 to 1.0 (cation exchange capacity divided by anion exchange capacity) (Kelley, 1948). While the edge surface in kaolinite is more important than planar surfaces as a source of charge, the reverse is true in montmorillonite. However, the greater total surface exposed by the smaller montmorillonite particles balances their comparative anion exchange capacities on a gravimetric basis. That is, 1 gram of montmorillonite, which has about an acre of total surface area, may have the same anion exchange capacity as a gram of kaolinite, in spite of the dominance of edge surfaces in the kaolinite.

The montmorillonite minerals are highly responsive to chemical environments, probably because of their colloidal size and structural peculiarities. A stable dispersion of this type mineral produces a high colloidal yield. It is likely that provision of a proper sodium environment is sufficient to enhance the inherent negativity of the montmorillonite particles to a point of adequate dispersion.

ILLITE

Illite includes a broad group of micalike clay minerals which to date have not been subdivided. Illites, like micas and montmorillonites are 2:1 layer minerals; that is, two silica tetrahedra units enclose one octahedral unit. Illites, however, differ from the mica minerals in several ways: in illites one-sixth of the Si^{++++} ions are replaced by Al^{+++} ions whereas in true micas one-fourth of the Si^{++++} ions are so replaced; the unbalanced cation deficiency is less, being 1.3 per unit cell as contrasted to 2.0 in micas; less potassium is adsorbed in interface position in illites but some Ca^{++} and Mg^{++} ions are adsorbed. Particles of illite generally are small, less than 1 to 2 microns. This may be attributed to weaker bonding brought about by less fixed K^+ in interface positions.

Illites generally as the fine-grained component of marine shales and are not as free from mineral contamination as the other two clay groups. Whereas the kaolinite and montmorillonite minerals used in the present study may be considered monomineralic, the illitic mineral is polymineralic, because of its intimate mixture with shale fragments.

The previously mentioned cation deficiency gives illite a weak negative charge, as indicated by its cation exchange capacity of but 10-40 milliequivalents per 100 grams. Anion exchange occurs at edge surfaces, and the ratio of cation to anion exchange capacities is approximately 2.3 to 1.0 (Kelley, 1948). One may postulate that dispersion characteristics of illite are somewhere between those of kaolinite and montmorillonite. If so, it should be possible to effect moderate deflocculation of illite particles by anion adsorption at clay edges and by increasing inherent negativity through replacement of adsorbed Ca^{++} and Mg^{++} ions by Na^+ ions.

DISCUSSION OF THE HYDROMETER METHOD

By I. S. McQUEEN

The hydrometer has been used extensively as a means of determining the particle-size distribution of soils and sediments. Like most methods of wet mechanical analysis, the hydrometer method is based on Stokes' law, defined in 1845 by Sir George Stokes, a British mathematician and physicist. Stokes' law states that the terminal fall velocity of a solid spherical particle in quiet water is defined by the following relation:

$$V = \frac{2}{9} gr^2 \frac{\rho - \rho_0}{\mu}$$

Where

V =velocity of fall in centimeters per second
 g =acceleration due to gravity (981 centimeters per second squared)

r =radius of particle in centimeters

ρ =density of particle in grams per cubic centimeter

ρ_0 =density of fluid in grams per cubic centimeter

μ =viscosity of fluid in poises (dyne-second per square centimeter)

If a point is chosen at a given depth, H (centimeters), and time, t (minutes), after mixing in a column of uniform spherical particles dispersed in water (for which $\rho_0=1$), the above expression can be solved for the diameter of the coarsest particle remaining in suspension at the given depth and time. Substituting $V = \frac{H}{60t}$ and $r = \frac{d}{20}$ for time in minutes and diameter of particle in millimeters, gives:

$$d = \sqrt{\frac{30H\mu}{g(\rho-1)t}}$$

There are several requirements in any method that uses Stokes' law to determine the diameter of particles:

1. The depth of fall, H , must be defined and measurable.
2. The density and viscosity of the fluid must be constant and known.
3. The specific gravity of the particles must be known.
4. The particles should be spherical.
5. The concentration of particles in suspension should be low enough to minimize the interference between particles yet high enough to produce measurable differences in the specific gravity of the suspension.
6. The particles must be completely dispersed as discrete particles and must remain so throughout the test.

In standard hydrometer analysis methods, these conditions are all assumed to have been met. Krynine (1941, p. 477) describes the theory of grain-size measurement with a hydrometer as follows:

Since at the start of the hydrometer test the suspension is thoroughly mixed there are, at each horizontal section of the graduate, particles of all sizes present in the given sample in their natural concentration. As sedimentation proceeds, all grains of a given diameter settle with equal velocity; hence their concentration at all horizontal sections of the graduate is the same. Owing to the limited supply of particles from above, coarser particles gradually fall out. Thus at a given time moment there are at a given horizontal section of the graduate, particles finer than a given diameter only, though in their natural concentration.

A hydrometer consists of a hollow glass chamber or bulb, weighted at the bottom and having a graduated stem at the top. It has a constant mass, and when placed in a liquid it sinks until it displaces its own weight of liquid.

In conventional hydrometer analyses the depth of fall of a particle is assumed to be the distance from the water surface to the center of the hydrometer bulb. The hydrometer, however, does not measure the specific grav-

ity of the fluid or suspension at a point (Puri, 1949, p. 245). It averages the specific gravity in a zone, the nature of which depends upon the shape and depth of submergence of the hydrometer. This characteristic of the hydrometer may bring errors into an analysis.

ADVANTAGES OF THE HYDROMETER METHOD

Two important advantages of the hydrometer method over other types of wet mechanical analysis are its convenience and the rapidity with which observations can be made. Results are available as soon as the settling time for the smallest size fraction to be determined has passed. There is no problem of evaporating large numbers of samples to dryness. Each point on the size distribution curve, or each size fraction to be determined, merely requires that a reading be made of the hydrometer at a specified time.

There is also a saving in space and equipment, because the hydrometer method does not require the pipette rack, drying oven, balance, and evaporating dishes that are used in the pipette method.

Another advantage of the hydrometer method is that the sample remains intact. There is no removal of parts of the sample as the test proceeds. This makes it possible to use the same sample for successive increments of deflocculents, resulting in a saving in time and material and eliminating some inaccuracies resulting from differences in samples. It is not necessary to prepare and disperse a separate sample for each increment of deflocculent. In the present work it was desirable and important that the sample remain intact so that successive amounts of deflocculent could be added to the same sample. If it had been necessary to use separate samples, small differences among samples possibly could have masked the effects of the deflocculent.

DISADVANTAGES OF THE HYDROMETER METHOD

The theory of hydrometer analyses assumes that the density of the suspension is being measured at a point. Actually, the hydrometer averages the specific gravity in a zone. If the specific gravity varied uniformly through the measured zone, the value at the center of the zone and the average value would coincide. This is generally true with materials that have a wide distribution of grain sizes in suspension. In suspensions with a narrow range of grain size the average density through the measured zone may not be the same as the density at the center of the hydrometer.

The exact nature of the zone measured by a given hydrometer can be determined by a simple experiment. From a balance, suspend a hydrometer in a hydrometer jar or cylinder. Gradually fill the hydrometer jar with water and record the weight of the hydrometer and the

depth of submergence at small intervals. Curve *a* of figure 48A is a plot of the data that may be obtained from such an experiment. The relative buoyancy of the hydrometer at each horizontal section will be a function of the rate of change of hydrometer weight with depth of submergence and hence will be a function of the slope of curve *a*. Curve *b* of figure 48A is derived from curve *a*¹ and represents the relative buoyancy of the fluid on the hydrometer at each horizontal section.

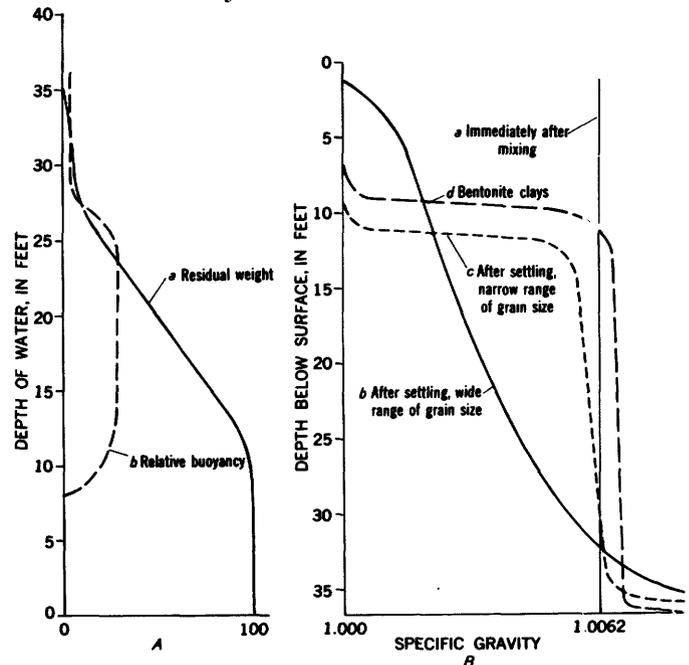


FIGURE 48.—Nature of zone measured by a hydrometer. *A*, diagrammatic representation of zone 1 measured by hydrometer; *B*, hypothetical curves illustrating different types of suspensions.

Figure 48B represents the theoretical distribution of specific gravities of different types of suspensions in a hydrometer jar. Curve *a* shows a suspension immediately after mixing. Curve *b* represents a material with a wide range of grain sizes after a period of settling. On this curve, if the specific gravities are averaged over the zone measured by the hydrometer, a value is obtained that is very near the value at the depth of the center of the hydrometer bulb. Curve *c* represents a material with a very narrow range of grain sizes. If the particles are discrete they all have about the same settling velocity and clear solution is left above them. If the hydrometer measured the specific gravity at a fixed point, the readings would change from maximum to a minimum almost immediately as the last particles pass the measuring point. However, as the hydrometer measures a zone and also sinks deeper as the particles settle, it takes an appreciable time interval

¹ Curve *b* of figure 48A represents the cosine of the angle between curve *a* and the *x*-axis plotted against the depth. Curve *b* also corresponds to the shape of the hydrometer used and defines the zone measured by it.

for the readings to change and the grain size distribution curve may be distorted. The materials used in this investigation tend toward narrow ranges of grain sizes, and hence may have distorted grain size distribution curves. Montmorillonite clays seem to be special in that, under certain conditions, they do not settle as discrete particles but form loose floc structures that undergo consolidation. This condition is represented by curve *d* and the anomalous results obtained from it are discussed more fully in the section on tables of data and dispersion indices.

The behavior of the hydrometer in suspensions with a narrow range of grain sizes is the principal disadvantage in the method. This disadvantage was minimized in the current investigations, because it was not pertinent to determine the grain size of discrete particles. The purpose of the investigation was to measure differences in dispersion characteristics and the hydrometer method proved to be well suited for this purpose.

THEORY OF CLAY MINERAL BEHAVIOR IN DILUTE SUSPENSIONS

By R. F. MILLER

The primary objectives of a canal sedimenting program are to transport the clay material by canal waters to the areas where seepage losses occur and to allow the clay material to penetrate and seal the openings through which seepage takes place.

The efficiency of clay transport and penetration is a function of the effective size of the clay materials. The effective size of clay particles suspended in water may vary with the type of clay and the chemical environment in the water system.

One of the objectives of this investigation was to study the dispersion characteristics of three basic types of clay minerals in waters of different chemical composition. These characteristics are a function of physico-chemical reactions in the clay-water system. A brief review of the interactions operative in a clay-water system follows. It is presented here as a guide to evaluating the observations on clay-water systems noted during the study.

The dispersion of clays in water involves the separation of the clays into their finest discrete particles and maintaining them in suspension. Clays that are dispersed can be transported more easily by water and can penetrate small voids more readily. A dispersed clay-water system is related to the physical law that like charges repel and unlike charges attract.

There are many theories on the mechanism of dispersion. The discussion that follows is a composite of

these theories that explains the observations made during this investigation.

The various clay minerals are negatively charged to some degree. The mechanism of the dispersion of clay particles in water is a function of this negative charge.

The literature on clay minerals generally attributes the negative charge on the surface of clay particles to isomorphous substitution, dissociation of lattice hydroxyl (OH^-) ions, and anion adsorption.

Isomorphous substitution is the substitution of ions of similar size for each other during the formation of the crystal lattice of a clay mineral. An example of isomorphous substitution is the substitution of divalent magnesium (Mg^{++}) ions for trivalent aluminum (Al^{+++}). This type of substitution results in an imbalance of positive and negative charges within the structure of a clay particle yielding a cation deficiency and a negative charge expressed at the surface. The intensity of this negative charge is proportional to the amount of cation deficiency resulting from isomorphous substitution. This influences the number of cations that are adsorbed to each clay particle to balance the negative charge. Isomorphous substitution is discussed in more detail by Marshall (1949), Grim (1953), and Kelly (1948).

Dissociation of lattice OH^- ions as a source of negative charge for clay particles is summarized by Russell (1950, p. 117) as "Negative charges developed by hydrogen ions dissociating from hydroxyls attached to silicon atoms at the broken edges of oxygen sheets, which compose the clay mineral." This reaction can be written, $\text{Si}-\text{OH} + \text{H}_2\text{O} \rightarrow \text{Si}-\text{O}^- + \text{H}_3\text{O}^+$. It only occurs appreciably under neutral or alkaline conditions, and the more alkaline the conditions the greater is the negative charge developed.

Anion adsorption is the electrostatic attraction of negatively charged anions to positively charged cations exposed at the broken edges of clay particles. This reaction adds to the total negative charge expressed at the surface of clay particles, if the adsorbed anion is more highly charged than the attracting cation. This source of charge is discussed in more detail by Ruehrwein (1953) and Olphen (1950).

FACTORS THAT CONTROL THE DEGREE OF DISPERSION

If negatively charged clay particles and distilled water were the only components of a clay-water system, the system would be easy to understand. The negatively charged particles would repel each other and disperse throughout the system, since like charges repel. Also, since water molecules tend to be positive at one end and negative at the other, they could be expected to orient themselves about the charged clay particles

in concentric shells. The water shells could act as barriers between particles and the net result would probably be a dispersed system. However, a clay-water system is not this simple, for water contains salts in solution which ionize into positively charged cations such as calcium (Ca^{++}), magnesium (Mg^{++}), and sodium (Na^+), and negatively charged anions such as chloride (Cl^-), sulfate (SO_4^{--}), and phosphate (PO_4^{---}). These charged ions react with the clay, the water, and each other and complicate clay dispersion.

The maintenance of a dispersed system or a degree of dispersion in a complex clay, water, ionized salt system may be described as control of repelling and attracting forces. These forces are affected by:

1. The negative charge of the clay particle.
2. The valence or negative charge carried by the anions in the solution.
3. The valence or positive charge carried by the cations in the solution.
4. The concentration of the cations in solution.
5. Hydration of ions in solution.
6. The mobility of the cations in solution.
7. Osmotic pressure differences in the clay-water system.

Any one or all of these factors could influence dispersion when a clay is placed in a canal water in a sediment-lining operation. A discussion of each of the above factors follows:

Negative charge on the surface of clay particles.—The negative charge on the surface of clay particles provides a repellent force between clay particles but also attracts and holds the exchangeable cations. The quantity of exchangeable cations associated with a clay particle is directly proportional to the negative charge of the particle. The clays in order of magnitude of the negative charge expressed at their surfaces are: (a) montmorillonite, (b) illite, (c) kaolinite. To illustrate the magnitude of the attractive force that may be expressed on a single clay surface, Kelley (1948) estimates that a montmorillonite-type clay (bentonite) with plate dimensions of $1 \mu \times 0.4 \mu$ could have about 600,000 exchangeable monovalent ions per lattice layer. This type of clay would have an exchange capacity of approximately 1 milliequivalent per gram of clay and 1 milliequivalent of a monovalent ion such as sodium, contains 6.023×10^{20} ions.

Valence of the negative ions (anions).—The negative valency of the anions in solution in a complex clay, water, ionized salt system may affect the control of dispersion in the system. Polyvalent anions may replace anions with less charge from anion exchange

positions at the broken edges of clay particles, thus increasing the negative charge.

Multivalent anions may add a negative charge to a clay particle but no charge is added by monovalent anions. Only part of the negative charge associated with a multivalent anion is used by attraction to the exposed cation. The increase in dispersion potential of a clay-water system through the absorption of negatively charged ions on the clay particle is roughly proportional to the unused valency of the anions. For example, much more negative charge would be added to a clay surface by the adsorption of a long chain polyanion of high negative valence than by the adsorption of a simple anion, such as orthophosphate (PO_4^{---}).

Valence of the positive ions (cations).—The positive valency of the cations is also an important factor in the control of dispersion in a clay, water, ionized salt system.

The cations attracted to a negatively charged clay particle form a positively charged shell or cloud around each clay particle. The attracted cations tend to form two layers about each particle, a closely held inner layer and a more loosely held or diffuse outer layer. The diffuseness or depth of the outer layer or cloud of cations is related to the charge or valency of its component cations. Multivalent cations are more strongly attracted to the clay than are monovalent cations; therefore, an outer shell of monovalent cations is more diffuse than one of multivalent cations. This results in a shell or barrier of positively charged monovalent ions at greater distance from the clay particle than when multivalent cations comprise the shells.

The shells of positively charged ions surrounding each clay particle in a clay-water system tend to repel one another. Therefore, the diffuseness of the outer ring of associated cations is an important factor in the control of clay dispersion in a clay, water, ionized salt system. Generally, the greater the diffuseness of the clouds of cations about each clay particle in the system, the greater the dispersion in the system.

Concentration of the cations in solution.—The concentration of the cations in solution in a clay-water system is another of the factors that controls the depth of the diffuse shell of cations that surround a clay particle. Increasing the concentration of positively charged ions crowds more cations into the zone between clay particles and, in effect, helps to neutralize the negative charge of a clay particle closer to the particle. This in turn decreases the diameter, or depth of the shells of positive ions surrounding the clay particles. Thus, dispersion in a clay, water, ionized salt system may be reduced by decreasing the diameter of the repelling shells of cations about each clay particle through increased cation concentration.

Conversely, Bolt,² found that dispersion of the system may be obtained even if Ca^{++} or Mg^{++} are the dominant ions, but that the concentration of these ions in the system must be much more dilute to achieve dispersion than is necessary when Na^+ is the predominant ion in solution.

Hydration of cations in solution.—The hydration of cations in solution is the result of electrostatic attraction of concentric shells of dipole water molecules about each cation. These shells of dipole water molecules vary in depth with the size, valency, and mobility of the cations. If cations become hydrated the shells of water may affect the efficiency of their positive charge, for the intensity of an electrostatic charge varies inversely with the square of the distance from the source of the charge. For example, if two cations of equal charge were hydrated to different degrees, the cation with the smaller shell of attracted water would be the more efficient in neutralizing the negative charge of a clay particle in a clay-water system. Thus, hydration along with valency and concentration may affect the diffuse cloud of cations about each clay particle and affect control of dispersion.

Mobility of the cations in solution.—The mobility of the cations in solution in a clay-water system may also affect the diffuseness of the repelling shell or cloud of cations about each clay particle. The mobility of a cation in solution may be considered as the speed with which the cation moves or oscillates about in solution. A highly mobile cation such as sodium may not be as easily attracted to a negatively charged clay particle as a less mobile cation such as calcium or magnesium. Therefore, mobility could effect the efficiency with which a cation neutralized the negative charge of the clay particle. This may result in diffuse shells of cations about each of the clay particles and thus influence the control of dispersion in a clay-water system.

Osmotic pressure.—Osmotic pressure may aid in attaining dispersion in a clay-water system. The concentration of ions in the diffuse cloud of ions around each clay particle is greater than the concentration of ions in the part of the solution not affected by electrostatic forces from the clay particles. There is a tendency for ions in solution to come to equilibrium and eliminate differences in concentration. While the two systems are attempting to reach equilibrium, convection currents may be set up which could aid the other forces in the system in attaining dispersion. This aid to dispersion would no longer exist after equilibrium had been attained.

²Bolt, G. H., 1954, Physico-chemical properties of the electric double layer on planar surfaces: Ph. D. thesis, Cornell Univ., Ithaca, N. Y., 106 p.

Forces other than those mentioned here may be effective in controlling dispersion in a clay, water, ionized salt system, but those discussed are perhaps the most dominant interacting in the systems studied in these experiments.

DISPERSION AND CLAY MINERALS

Montmorillonite, "illite", and kaolinite are the three dominant clay-mineral types that may be available for sediment-lining operations. Each of the above clays has associated with it some negative charge. The negative charge of clay particles affects the degree to which they may be dispersed in a clay-water system. As previously stated, three sources of negative charge on clay surfaces are isomorphous substitution (cationic deficiency), dissociation of lattice hydroxy (OH^-) ions, and anion adsorption. These sources of negative charge may be common to all types of clay but are effective to different degrees.

Montmorillonite-type clays.—Montmorillonite-type clays are more highly charged and finer textured than the other two clays. Isomorphous substitution is the predominant source of the negative charge on montmorillonite-type clays. Grim (1953, p. 132) attributes about 20 percent of the exchange capacity to broken bonds. This includes possible negative charge from dissociation of lattice OH^- ions, or adsorption of high valence anions. Because of the more intense negative charge and finer texture associated with montmorillonite-type clays, a higher degree of dispersion is possible with them than with other types of clay.

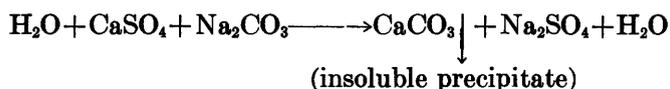
Kaolinite-type clays.—The predominant source of negative charge on kaolinite-type clay minerals is unsatisfied chemical bonds at the broken edges, or from dissociation of H^+ from exposed OH^+ groups or the octahedral (alumina) sheet. The negative charge may also be increased through the adsorption of high valence negative ions to positive ions exposed at the broken edges. Since the anion exchange capacity of kaolinite particles is equivalent to the cation exchange capacity, it is logical that the dispersibility of kaolinite could readily be influenced by the valence of the anions injected into the clay-water system.

Illite-type clays.—The dispersion characteristics of illite-type clays should be intermediate between those of montmorillonite- and kaolinite-type clays. The negative charge on the surface of illite-type clays is the result of both isomorphous substitution and anion adsorption at the broken edges. Illite clays are generally components of shales and are less likely to be monomineralic than are montmorillonite and kaolinite deposits, therefore, the characteristics of this type of material are more difficult to evaluate or predict.

MECHANISM OF DISPERSION CONTROL

Since a dispersed clay-water system may be more readily obtained with Na^+ as the dominant cation in the system, most dispersion controls involve deactivation or removal of Ca^{++} and Mg^{++} from the clay-water system and replacement with Na^+ ions.

Calcium and magnesium ions may be removed from a clay-water system by causing them to form insoluble precipitates and to settle out of the system. This may be accomplished by adding Na_2CO_3 to the system. For example, if calcium were in the system as CaSO_4 and Na_2CO_3 were added to the system, the salts would react according to the following equation:



Since calcium is precipitated, no equilibrium could be maintained and most of the calcium could be removed from solution. The settling of the precipitate thus formed to the canal bottom could hinder the penetration and sealing action of clay. To avoid this it is possible to cause the Ca^{++} and Mg^{++} ions to lose their identity as active cations by causing them to become part of a complex phosphate anion. This process is known as sequestration.

Through the mechanism of sequestration, Ca^{++} and Mg^{++} ions that can quite effectively neutralize the negative charge on clay particles and cause flocculation³ in a clay, water, ionized salt system lose their identity as cations and subsequently lose their positive charge by becoming part of a complex anion.

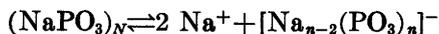
Concurrent with the removal of calcium and magnesium from the solution as active ions, amounts of sodium from the sodium polyphosphates may be released into the clay, water, ionized salt system.

The amount of calcium that may be sequestered by a dehydrated sodium phosphate is related to the dissociation of Na^+ , and its replacement by Ca^{++} or Mg^{++} .

The dehydrated sodium phosphates do not dissociate completely when dissolved in water as do salts such as sodium chloride. Sodium chloride dissociates as follows:



All of the Na^+ ions in sodium chloride immediately ionize and are available for reactions. According to Daugherty (1948) sodium hexametaphosphate ionizes or dissociates in two steps as follows:



³ Bolt (1954) presented evidence that the binding force among particles within a floc may be the attraction of positive ions exposed at broken edges to the negative surfaces, but that these attractive forces are too small to be effective until most of the negative charge on the clay surface has been equalized by the introduction of sufficient quantities of cations into the system.

and possibly a secondary ionization as follows:



This dissociated sodium is available to react with the clay, water, ionized salt system. If Ca^{++} or Mg^{++} are present they replace the dissociated Na^+ and the equilibrium reverses to form $\text{Ca Na}_{n-2}(\text{PO}_3)_n$ or $2 \text{Ca Na}_{n-4}(\text{PO}_3)_n$. Which complex salt is formed is a function of the concentration of Ca^{++} and Mg^{++} in the system. The other dehydrated sodium phosphates tested, dissociate and sequester in a similar manner. The net result is a more dispersed system through the mechanisms previously described. This may not always hold true, for if the initial salt concentration in the system is such that even the less effective Na^+ ions neutralize the negative charge close to the clay surfaces, the clay-water system will remain flocculated; as occurred in the soft water used in the first year's study.

Aside from the sequestration of Ca^{++} and Mg^{++} as a part of complex anions, these anions affect the total negative charge on the clay particles in a clay, water, ionized salt system. As previously discussed, anions may be attracted to incompletely neutralized positive ions exposed at the broken edges of clay particles. If the absorbed negative ion is a long chain polyanion, it could be attracted to the clay particle by a fraction of its negative valency. The net result could be the addition of a strong negative charge to the clay particle, thus increasing the dispersion potential of the system. This would increase the negative charge proportionately more for kaolinite than for montmorillonite.

TABLES OF DATA AND DISPERSION INDICES

All of the base data obtained during this investigation are contained in tables 2 to 19. Each table includes the data for a specific combination of colloid and deflocculent. Soft water refers to a synthetic water having a content of calcium, magnesium, and sodium of 3, 2, and 15.5 milliequivalents per liter, respectively. Hard water refers to a synthetic water having a content of calcium, magnesium, and sodium of 17, 8, and 17 milliequivalents per liter, respectively.

Ion saturation.—This column designates the ion saturation on the colloid prior to its introduction into the system.

Grams deflocculent.—The total amount of deflocculating chemicals in the system is listed for each hydrometer test run.

Percent in suspension.—In these columns are listed the amounts of colloid remaining in suspension at the given times following mixing as indicated by the hydrom-

eter reading corrected for the hydrometer reading in the check cylinder. These amounts are listed as percentages of the colloid originally introduced into the system. With montmorillonite, these percentages occasionally exceed 100 because of the anomalous behavior of this clay in dilute suspensions. The loose floc structure formed by some suspensions of montmorillonite seems to consolidate instead of settle as discrete particles. If the zone measured by the hydrometer is within the consolidated portion of a cylinder of this suspension it will measure a higher concentration of clay than the original freshly mixed sample contained. Percentage values in parentheses were obtained by extrapolation. Approximate grain size being measured at each time in a normal hydrometer grain size analysis is:

Time in minutes.....	1	4	19	60	435	1,545
Approximate grain size in microns.....	37	19	9	5	2	1

These grain sizes have no literal significance in the current investigations and should be used only as a guide in plotting the hydrometer data for comparison purposes.

The column headed "sum" is the sum of the percentages in suspension as listed in the preceding six columns. This sum was used in computing the dispersion indices.

Dispersion index.—This column lists a percentage comparison between the given sample run and a standard. This is described and discussed in a previous section of this report.

TABLE 2.—Hydrometer data: Montmorillonite and sodium tripolyphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	91	90	86	92	90	90	529	100.9
Do.....	.025	98	96	96	99	98	97	584	109.7
Do.....	.1	101	99	99	99	100	96	584	111.7
Calcium.....	.0	74	54	28	11	(4)	(2)	173	32.5
Do.....	.05	84	67	38	4	(2)	(0)	185	36.6
Do.....	.1	82	70	10	7	(3)	(1)	173	32.5
Do.....	.3	80	72	46	34	24	(14)	279	50.8
Do.....	.5	90	83	69	69	52	41	404	75.9
Do.....	1.0	87	86	86	85	82	73	499	93.8
Do.....	1.5	87	86	89	88	87	82	519	97.6
Soft water									
Sodium.....	0.0	102	102	106	100	103	(100)	613	115.2
Do.....	.025	99	98	102	102	103	108	612	115.0
Do.....	.1	96	96	101	102	97	(97)	589	110.7
Calcium.....	.0	74	54	34	8	0	(0)	170	32.0
Do.....	.025	81	65	44	15	(5)	(3)	213	40.0
Do.....	.1	82	66	47	7	(3)	(1)	206	38.7
Do.....	.5	83	71	68	54	34	(14)	324	60.9
Do.....	1.0	96	92	91	88	80	70	517	97.2
Do.....	1.5	97	97	97	95	92	79	557	104.7
Do.....	2.0	91	91	91	91	89	86	539	101.3
Hard water									
Sodium.....	0.0	82	81	80	86	85	4	418	78.6
Do.....	.05	88	88	88	89	(80)	(18)	451	84.8
Do.....	.1	84	86	86	84	(74)	(6)	420	78.9
Do.....	.5	85	85	85	86	(60)	(2)	403	75.8
Do.....	1.0	82	82	79	82	(80)	(5)	410	77.1
Do.....	2.0	85	85	76	76	83	(47)	452	85.0
Do.....	3.0	96	96	96	96	85	(11)	480	90.2
Do.....	4.0	94	94	94	94	89	52	517	97.2
Calcium.....	.0	80	72	1	0	(0)	(0)	153	28.8
Do.....	.025	84	72	1	(0)	(0)	(0)	157	29.5
Do.....	.05	84	71	1	(0)	(0)	(0)	156	29.3
Do.....	.1	86	75	2	(1)	(0)	(0)	164	30.8
Do.....	.3	86	70	1	(0)	(0)	(0)	157	29.5
Do.....	.5	85	73	13	(7)	(0)	(0)	178	33.5
Do.....	1.0	80	75	64	24	12	(0)	235	47.9
Do.....	2.0	82	78	79	74	55	37	405	76.1
Do.....	3.0	94	94	94	94	92	78	546	102.6

¹ At 4,320 minutes=71 percent; at 5,760 minutes=64 percent.

TABLE 3.—Hydrometer data: Montmorillonite and sodium hexametaphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	89	87	89	89	90	86	530	99.6
Do.....	.025	98	96	99	97	97	95	582	109.4
Do.....	.1	99	96	97	97	99	96	584	109.8
Calcium.....	.0	72	51	26	10	(5)	(0)	164	30.8
Do.....	.05	75	69	42	26	(13)	(0)	225	42.3
Do.....	.1	78	65	48	36	(24)	(12)	262	49.2
Do.....	.3	82	70	60	50	36	(24)	322	60.5
Do.....	.5	83	75	68	62	52	43	383	72.0
Do.....	1.0	83	81	81	78	77	62	462	86.8
Do.....	1.5	92	83	90	90	84	77	516	97.0
Soft water									
Sodium.....	0.0	98	97	100	93	99	(98)	585	110.0
Do.....	.025	93	93	96	97	95	100	574	107.9
Do.....	.1	91	90	93	90	(80)	(75)	519	97.6
Calcium.....	.0	78	59	36	11	2	(1)	187	35.2
Do.....	.025	81	66	45	11	(5)	(1)	209	39.3
Do.....	.1	84	69	48	6	(3)	(0)	210	39.5
Do.....	.5	86	76	67	58	8	(4)	299	56.2
Do.....	1.0	94	83	78	79	58	53	445	83.6
Do.....	1.5	99	99	88	86	73	61	506	95.1
Do.....	2.0	89	89	89	88	82	¹ 72	509	95.7
Hard water									
Sodium.....	0.0	85	85	85	85	79	34	453	85.2
Do.....	.05	88	88	88	74	(70)	(25)	433	81.4
Do.....	.1	86	86	86	83	(80)	(30)	451	84.8
Do.....	.5	86	86	86	86	(80)	(40)	464	87.2
Do.....	1.0	82	81	82	80	(75)	(25)	425	79.9
Do.....	2.0	86	86	86	86	(80)	(40)	464	87.2
Do.....	3.0	96	96	96	96	85	(50)	519	97.6
Do.....	4.0	93	93	96	88	86	85	541	101.7
Calcium.....	.0	92	82	8	2	(1)	(0)	185	34.8
Do.....	.025	92	81	8	5	(3)	(0)	189	35.5
Do.....	.050	89	(75)	5	(3)	(0)	(0)	172	32.4
Do.....	.1	94	74	4	(2)	(0)	(0)	174	32.7
Do.....	.3	89	70	6	5	(3)	(0)	173	32.5
Do.....	.5	93	70	6	(3)	(0)	(0)	172	32.3
Do.....	1.0	94	84	21	8	(4)	(0)	211	39.7
Do.....	2.0	98	90	77	58	12	(6)	341	64.1
Do.....	3.0	96	96	91	44	44	18	418	78.6
Do.....	4.0	75	75	74	74	68	8	374	70.3
Do.....	5.0	59	59	58	58	67	65	366	68.8

¹ At 4,320 minutes=61 percent; at 5,760 minutes=58 percent.

TABLE 4.—Hydrometer data: Montmorillonite and sodium hexametaphosphate plus sodium carbonate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	88	88	89	88	88	89	530	99.6
Do.....	.025	98	96	98	98	98	96	584	109.8
Do.....	.1	98	97	97	98	98	96	584	109.8
Calcium.....	.0	72	59	32	16	(8)	(0)	187	35.2
Do.....	.05	78	62	42	26	(13)	(7)	228	42.9
Do.....	.1	81	70	51	35	(18)	(9)	264	49.6
Do.....	.3	76	67	52	41	28	(20)	284	53.4
Do.....	.5	89	81	69	59	49	37	384	72.2
Do.....	1.0	86	83	81	76	68	58	452	85.0
Do.....	1.5	87	85	86	85	82	76	501	94.2
Soft water									
Sodium.....	0.0	102	102	103	102	104	(102)	615	115.6
Do.....	.025	98	98	102	104	101	108	611	114.8
Do.....	.1	100	99	104	104	103	105	615	115.6
Calcium.....	.0	76	57	33	12	0	(0)	17 ²	33.5
Do.....	.025	79	59	40	7	(4)	(0)	189	35.5
Do.....	.1	77	62	38	3	(2)	(0)	182	34.2
Do.....	.5	85	70	54	27	0	(0)	236	44.4
Do.....	1.0	86	78	68	61	25	2	320	60.2
Do.....	1.5	95	95	91	88	76	60	505	94.9
Do.....	2.0	90	88	88	86	83	176	511	96.1
Hard water									
Sodium.....	0.0	86	86	86	91	4	(2)	355	66.7
Do.....	.05	83	83	81	81	(7)	(2)	337	63.3
Do.....	.1	84	84	84	85	(12)	(6)	355	66.7
Do.....	.5	86	86	85	85	(20)	(4)	366	68.8
Do.....	1.0	90	90	90	90	(40)	(8)	40 ⁸	76.7
Do.....	2.0	83	83	83	83	(60)	(12)	404	75.9
Do.....	3.0	88	88	85	88	85	34	468	88.0
Do.....	4.0	93	91	85	82	75	0	426	80.1
Calcium.....	.0	83	74	3	0	(0)	(0)	160	30.1
Do.....	.025	80	72	0	(0)	(0)	(0)	152	28.6
Do.....	.05	84	(73)	0	(0)	(0)	(0)	157	29.5
Do.....	.1	82	75	0	(0)	(0)	(0)	157	29.5
Do.....	.3	84	73	0	(0)	(0)	(0)	157	29.5
Do.....	.5	82	73	0	(0)	(0)	(0)	155	29.1
Do.....	1.0	83	77	51	0	(0)	(0)	211	39.7
Do.....	2.0	89	87	80	62	0	(0)	318	59.8
Do.....	3.0	100	100	90	76	56	0	422	79.3
Do.....	4.0	73	73	72	71	71	69	429	80.6
Do.....	5.0	59	59	57	57	68	68	368	69.2

¹ At 4,320 minutes=58 percent; at 5,760 minutes=55 percent.

TABLE 5.—Hydrometer data: Kaolinite and sodium tripolyphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	90	88	86	80	58	49	451	99.6
Do.....	.025	92	92	90	85	66	56	481	106.2
Do.....	.1	99	97	95	86	68	55	500	110.4
Calcium.....	.0	68	17	0	0	(0)	(0)	85	18.8
Do.....	.05	80	64	14	5	(3)	(2)	168	37.1
Do.....	.1	83	34	8	8	(4)	(2)	139	30.7
Do.....	.3	75	30	26	21	16	(11)	179	39.5
Do.....	.5	85	74	64	55	39	29	346	76.4
Do.....	1.0	90	88	83	73	57	45	436	96.2
Do.....	1.5	88	91	86	73	58	46	442	97.6
Soft water									
Sodium.....	0.0	91	80	7	7	(6)	(5)	196	43.3
Do.....	.025	95	92	30	6	(3)	(0)	226	49.9
Do.....	.1	97	96	58	13	7	(4)	275	60.7
Do.....	.5	97	95	88	78	58	16	432	95.4
Do.....	.75	94	93	86	75	54	44	446	98.5
Do.....	1.0	97	95	87	77	58	45	459	101.3
Do.....	1.5	96	96	88	75	57	45	457	100.9
Calcium.....	.0	66	37	8	5	0	(0)	116	25.6
Do.....	.025	79	58	10	5	(0)	(0)	152	33.6
Do.....	.1	70	56	12	4	(2)	(1)	145	32.0
Do.....	.5	80	65	55	39	1	(0)	240	53.0
Do.....	1.0	96	93	84	71	54	49	447	98.7
Do.....	1.5	98	98	97	81	62	52	488	107.7
Do.....	2.0	91	89	89	82	62	¹ 53	466	102.9
Hard water									
Sodium.....	0.0	70	27	0	(0)	(0)	(0)	97	21.4
Do.....	.05	87	44	0	(0)	(0)	(0)	131	28.9
Do.....	.1	83	50	2	(0)	(0)	(0)	135	29.8
Do.....	.5	85	70	0	(0)	(0)	(0)	155	34.2
Do.....	1.0	82	75	0	(0)	(0)	(0)	157	34.7
Do.....	2.0	85	85	25	0	(0)	(0)	195	43.0
Do.....	3.0	96	91	77	21	5	(3)	293	64.7
Do.....	4.0	96	89	83	72	54	38	432	95.4
Calcium.....	.0	89	37	3	2	(0)	(0)	131	28.9
Do.....	.025	93	48	4	(2)	(0)	(0)	147	32.4
Do.....	.05	97	63	4	(2)	(0)	(0)	166	36.6
Do.....	.1	99	61	7	(4)	(0)	(0)	171	37.7
Do.....	.3	99	69	5	(3)	(0)	(0)	176	38.8
Do.....	.5	99	78	4	(2)	(0)	(0)	183	40.4
Do.....	1.0	97	81	4	2	(1)	(0)	185	40.8
Do.....	2.0	97	97	59	10	2	(1)	266	58.7
Do.....	3.0	94	94	94	78	54	41	455	100.4

¹ At 4,320 minutes=45 percent; at 5,760 minutes=40 percent.

TABLE 6.—Hydrometer data: Kaolinite and sodium hexametaphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0. 0	91	90	88	79	63	55	466	102. 9
Do.....	. 025	101	100	97	86	72	60	516	113. 9
Do.....	. 1	100	99	96	88	73	60	516	113. 9
Calcium.....	. 0	68	28	2	0	(0)	(0)	98	21. 6
Do.....	. 05	79	50	40	21	(10)	(0)	200	44. 2
Do.....	. 1	82	68	48	28	(15)	(10)	251	55. 4
Do.....	. 3	93	86	77	66	46	(35)	403	89. 0
Do.....	. 5	93	91	85	74	55	40	438	96. 7
Do.....	1. 0	87	86	81	69	55	42	420	92. 7
Do.....	1. 5	95	93	88	76	52	41	445	98. 2
Soft water									
Sodium.....	0. 0	91	82	4	3	(2)	(1)	183	40. 4
Do.....	. 025	94	92	80	7	(5)	(4)	222	62. 2
Do.....	. 1	95	93	78	13	6	(5)	290	64. 0
Do.....	. 5	93	91	87	78	34	4	327	85. 4
Do.....	. 75	92	91	86	76	50	7	402	88. 7
Do.....	1. 0	91	90	85	73	58	33	430	94. 9
Do.....	1. 5	92	86	84	73	56	43	434	95. 8
Calcium.....	. 0	50	34	12	7	2	(1)	106	23. 4
Do.....	. 025	62	47	15	6	(3)	(2)	135	29. 8
Do.....	. 1	58	47	11	6	(4)	(2)	128	28. 2
Do.....	. 5	67	59	51	39	3	(1)	220	48. 6
Do.....	1. 0	91	87	83	70	54	35	420	92. 7
Do.....	1. 5	99	99	86	78	60	49	471	104. 0
Do.....	2. 0	88	87	85	76	60	150	446	98. 4
Hard water									
Sodium.....	0. 0	82	33	0	(0)	(0)	(0)	115	25. 4
Do.....	. 05	85	39	0	(0)	(0)	(0)	124	27. 4
Do.....	. 1	82	40	0	(0)	(0)	(0)	122	26. 9
Do.....	. 5	86	48	0	(0)	(0)	(0)	134	29. 6
Do.....	1. 0	82	50	2	(0)	(0)	(0)	134	29. 6
Do.....	2. 0	86	72	8	(5)	(3)	(2)	176	38. 8
Do.....	3. 0	96	96	53	13	8	(6)	272	60. 0
Do.....	4. 0	90	83	83	67	10	5	338	74. 6
Calcium.....	. 0	92	33	8	3	(2)	(1)	139	30. 7
Do.....	. 025	99	61	8	4	(2)	(0)	174	38. 4
Do.....	. 05	98	(61)	3	(2)	(0)	(0)	164	36. 2
Do.....	. 1	95	62	3	(2)	(1)	(0)	163	36. 0
Do.....	. 3	98	59	7	6	(4)	(2)	176	38. 8
Do.....	. 5	98	62	4	(3)	(2)	(1)	170	37. 5
Do.....	1. 0	100	70	8	8	(7)	(6)	199	43. 9
Do.....	2. 0	99	90	11	11	12	(12)	235	51. 9
Do.....	3. 0	96	92	73	17	14	17	309	68. 2
Do.....	4. 0	75	75	72	30	8	10	270	59. 6
Do.....	5. 0	57	57	56	56	13	12	251	55. 4
Do.....	6. 0	45	44	43	43	40	6	221	48. 8

¹ At 4,320 minutes=40 percent; at 5,760 minutes=36 percent.

TABLE 7.—Hydrometer data: Kaolinite and sodium hexametaphosphate plus sodium carbonate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	89	88	83	73	57	53	443	97.8
Do.....	.025	97	97	95	85	66	57	497	109.7
Do.....	.1	97	96	93	87	67	55	495	109.3
Calcium.....	.0	68	26	4	(2)	(0)	(0)	100	22.1
Do.....	.05	77	57	35	20	(10)	(0)	199	43.9
Do.....	.1	82	66	47	33	(22)	(11)	261	57.6
Do.....	.3	85	72	57	46	27	(18)	305	67.3
Do.....	.5	94	89	78	65	46	30	402	88.7
Do.....	1.0	88	86	82	72	55	43	426	94.0
Do.....	1.5	90	89	82	72	55	43	431	95.1
Soft water									
Sodium.....	0.0	96	78	2	0	(0)	(0)	176	38.8
Do.....	.025	95	92	78	8	3	(0)	276	60.9
Do.....	.1	95	93	79	6	0	(0)	272	60.0
Do.....	.5	102	92	94	81	58	36	463	102.2
Do.....	.75	95	93	92	80	59	46	465	102.6
Do.....	1.0	98	93	90	80	58	47	466	102.9
Do.....	1.5	97	95	90	80	60	47	469	103.5
Calcium.....	.0	73	44	9	4	0	(0)	130	28.7
Do.....	.025	74	56	18	5	(0)	(0)	153	33.8
Do.....	.1	76	60	11	3	(0)	(0)	150	33.1
Do.....	.5	80	67	52	11	0	(0)	210	46.4
Do.....	1.0	89	75	63	55	42	30	354	78.1
Do.....	1.5	96	95	85	76	55	42	449	99.1
Do.....	2.0	97	91	88	74	57	47	454	100.2
Hard water									
Sodium.....	0.0	60	28	0	(0)	(0)	(0)	88	19.4
Do.....	.05	78	40	0	(0)	(0)	(0)	118	26.0
Do.....	.1	80	46	0	(0)	(0)	(0)	126	27.8
Do.....	.5	84	68	0	(0)	(0)	(0)	152	33.6
Do.....	1.0	83	69	1	(0)	(0)	(0)	153	33.8
Do.....	2.0	81	79	34	(10)	(0)	(0)	204	45.0
Do.....	3.0	88	80	64	53	5	(0)	290	64.0
Do.....	4.0	91	90	82	72	46	16	397	87.6
Calcium.....	.0	93	35	6	4	(3)	(2)	143	31.6
Do.....	.025	90	52	3	(2)	(1)	(0)	148	32.7
Do.....	.05	91	(52)	3	(2)	(1)	(0)	149	32.9
Do.....	.1	90	69	5	(3)	(1)	(0)	168	37.1
Do.....	.3	89	78	5	(3)	(0)	(0)	175	38.6
Do.....	.5	90	80	4	(2)	(0)	(0)	176	38.8
Do.....	1.0	89	87	23	0	(0)	(0)	199	43.9
Do.....	2.0	95	95	55	2	0	(0)	247	54.5
Do.....	3.0	100	100	95	65	6	0	366	80.8
Do.....	4.0	74	74	70	70	46	30	364	80.4
Do.....	5.0	61	61	57	57	50	36	322	71.1
Do.....	6.0	42	42	42	42	41	38	247	54.5

¹ At 4,320 minutes=36 percent; at 5,760 minutes=30 percent.

TABLE 8.—Hydrometer data: Illite and sodium tripolyphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium-----	0. 0	94	92	84	70	38	25	403	102. 0
Do-----	. 025	96	95	91	78	46	31	437	110. 6
Do-----	. 1	104	102	96	78	46	29	455	115. 2
Calcium-----	. 0	19	14	8	0	(0)	(0)	41	10. 4
Do-----	. 05	26	18	12	4	(2)	(0)	62	15. 7
Do-----	. 1	32	24	16	12	(6)	(4)	94	23. 8
Do-----	. 3	28	20	14	9	4	(2)	77	19. 5
Do-----	. 5	29	21	15	11	6	4	86	21. 8
Do-----	1. 0	28	18	14	9	6	0	75	19. 0
Do-----	1. 5	29	22	18	11	8	6	94	23. 8
Soft water									
Sodium-----	0. 0	90	89	62	16	(5)	(2)	274	66. 8
Do-----	. 025	93	91	77	24	6	(3)	274	74. 4
Do-----	. 1	94	93	68	20	7	(4)	276	72. 4
Do-----	. 5	93	68	12	12	4	(2)	191	48. 4
Do-----	. 75	92	30	11	8	8	6	155	39. 2
Do-----	1. 0	92	37	19	17	15	10	190	48. 1
Do-----	1. 5	93	93	86	68	39	23	402	101. 8
Calcium-----	. 0	52	34	18	7	0	(0)	111	28. 1
Do-----	. 025	63	44	20	5	(2)	(1)	135	34. 2
Do-----	. 1	58	42	21	3	(2)	(0)	126	31. 9
Do-----	. 5	57	23	5	2	0	(0)	87	22. 0
Do-----	1. 0	54	12	5	4	4	8	87	22. 0
Do-----	1. 5	72	57	44	32	21	19	245	62. 0
Do-----	2. 0	75	63	49	38	26	124	275	69. 6
Hard water									
Sodium-----	0. 0	81	74	26	3	(2)	(0)	186	47. 1
Do-----	. 05	85	67	33	0	(0)	(0)	185	46. 8
Do-----	. 1	78	66	36	0	(0)	(0)	180	45. 6
Do-----	. 5	83	64	2	(0)	(0)	(0)	149	37. 7
Do-----	1. 0	80	65	1	(0)	(0)	(0)	146	37. 0
Do-----	2. 0	85	37	0	(0)	(0)	(0)	122	30. 9
Do-----	3. 0	88	80	32	13	0	(0)	213	53. 9
Do-----	4. 0	83	83	80	56	38	27	377	92. 9
Calcium-----	. 0	43	39	9	2	(1)	(0)	94	23. 8
Do-----	. 025	46	36	13	(6)	(3)	(1)	105	26. 6
Do-----	. 05	45	41	18	(9)	(3)	(2)	118	29. 9
Do-----	. 1	46	41	18	(9)	(3)	(2)	119	30. 1
Do-----	. 3	48	43	4	(2)	(0)	(0)	97	24. 6
Do-----	. 5	47	40	2	(1)	(0)	(0)	90	22. 8
Do-----	1. 0	44	38	0	0	(0)	(0)	82	20. 8
Do-----	2. 0	48	45	3	2	0	(0)	98	24. 8
Do-----	3. 0	52	47	43	34	23	20	219	55. 4

¹ At 4,320 minutes=21 percent; at 5,760 minutes=20 percent.

TABLE 9.—Hydrometer data: Illite and sodium hexametaphosphate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	90	90	83	67	39	25	394	99.7
Do.....	.025	98	96	91	74	44	29	432	109.4
Do.....	.1	98	98	90	73	46	29	434	109.9
Calcium.....	.0	31	21	8	0	(0)	(0)	60	15.2
Do.....	.05	26	18	12	7	(4)	(2)	69	17.5
Do.....	.1	31	23	14	9	(5)	(3)	85	21.5
Do.....	.3	27	20	13	8	3	(2)	73	18.5
Do.....	.5	28	22	14	8	4	1	77	19.5
Do.....	1.0	23	15	9	4	0	2	53	13.4
Do.....	1.5	28	22	15	10	5	1	81	20.5
Soft water									
Sodium.....	0.0	94	91	64	12	(4)	(2)	267	67.6
Do.....	.025	94	90	82	42	1	(0)	309	78.2
Do.....	.1	93	90	84	52	5	(3)	327	82.8
Do.....	.5	96	94	90	73	37	16	406	102.8
Do.....	.75	94	92	91	71	38	23	409	103.5
Do.....	1.0	97	96	91	73	36	24	417	105.6
Do.....	1.5	97	95	90	74	43	27	426	107.8
Calcium.....	.0	58	37	18	8	0	(0)	121	30.6
Do.....	.025	65	46	19	6	(0)	(0)	136	34.4
Do.....	.1	65	45	16	4	(0)	(0)	130	32.9
Do.....	.5	64	44	23	13	0	(0)	144	36.4
Do.....	1.0	69	51	31	20	11	13	195	49.4
Do.....	1.5	77	60	41	29	22	19	248	62.8
Do.....	2.0	74	59	44	34	26	¹ 24	261	66.1
Hard water									
Sodium.....	0.0	70	59	17	0	(0)	(0)	146	37.0
Do.....	.05	86	85	43	4	(2)	(0)	220	55.7
Do.....	.1	82	82	40	2	(1)	(0)	207	52.4
Do.....	.5	85	84	42	4	(2)	(0)	217	54.9
Do.....	1.0	81	78	16	8	(4)	(0)	187	47.3
Do.....	2.0	86	86	33	14	(7)	(4)	230	58.2
Do.....	3.0	99	96	69	16	11	(9)	300	75.9
Do.....	4.0	99	96	83	35	10	12	335	84.8
Calcium.....	.0	42	39	9	0	(0)	(0)	90	22.8
Do.....	.025	47	39	20	2	(1)	(0)	109	27.6
Do.....	.05	40	(35)	12	(4)	(3)	(2)	96	24.3
Do.....	.1	38	33	9	(5)	(0)	(0)	85	21.5
Do.....	.3	40	34	8	2	(1)	(0)	85	21.5
Do.....	.5	42	40	2	(1)	(0)	(0)	85	21.5
Do.....	1.0	45	40	14	0	(0)	(0)	99	25.1
Do.....	2.0	43	37	15	6	7	(6)	114	28.9
Do.....	3.0	49	43	36	10	10	10	158	40.0
Do.....	4.0	39	35	31	14	4	6	129	32.7
Do.....	5.0	43	35	31	25	19	12	165	41.8
Do.....	6.0	35	31	28	20	16	12	142	35.9

¹ At 4,320 minutes=22 percent; at 5,760 minutes=20 percent.

TABLE 10.—Hydrometer data: Illite and sodium hexametaphosphate plus sodium carbonate

Ion saturation	Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
		1	4	19	60	435	1,545		
Distilled water									
Sodium.....	0.0	93	92	83	64	37	23	392	99.2
Do.....	.025	100	100	93	76	42	30	441	111.6
Do.....	.1	100	99	93	73	43	28	436	110.4
Calcium.....	.0	26	20	10	(5)	(3)	(0)	64	16.2
Do.....	.05	28	19	12	8	(5)	(1)	73	18.5
Do.....	.1	31	22	18	12	(8)	(6)	97	24.6
Do.....	.3	28	18	14	8	3	(2)	73	18.5
Do.....	.5	29	20	16	11	8	3	87	22.0
Do.....	1.0	26	17	13	8	6	3	73	18.5
Do.....	1.5	25	17	13	9	7	4	75	19.0
Soft water									
Sodium.....	0.0	91	87	65	9	(0)	(0)	252	63.8
Do.....	.025	88	85	78	28	(0)	(0)	279	70.6
Do.....	.1	88	84	80	51	0	(0)	303	76.7
Do.....	.5	91	88	85	66	18	2	350	88.6
Do.....	.75	90	87	85	67	30	15	374	94.7
Do.....	1.0	93	90	85	66	32	17	373	97.0
Do.....	1.5	94	92	84	68	35	20	373	99.5
Calcium.....	.0	58	37	16	7	0	(0)	118	29.9
Do.....	.025	61	38	15	4	(0)	(0)	118	29.9
Do.....	.1	58	38	12	2	(0)	(0)	110	27.8
Do.....	.5	67	46	20	8	0	(0)	141	35.7
Do.....	1.0	67	47	24	16	9	8	171	43.3
Do.....	1.5	74	52	31	22	13	11	203	51.4
Do.....	2.0	71	48	29	19	10	¹ 10	187	47.3
Hard water									
Sodium.....	0.0	76	70	24	0	(0)	(0)	170	43.0
Do.....	.05	80	78	40	0	(0)	(0)	198	50.1
Do.....	.1	78	74	47	0	(0)	(0)	199	50.4
Do.....	.5	83	83	52	0	(0)	(0)	218	55.2
Do.....	1.0	87	77	15	0	(0)	(0)	179	45.3
Do.....	2.0	83	75	3	(0)	(0)	(0)	161	40.8
Do.....	3.0	88	80	64	32	5	(0)	269	68.1
Do.....	4.0	88	85	72	56	22	3	326	82.5
Calcium.....	.0	36	33	5	0	(0)	(0)	74	18.7
Do.....	.025	34	30	10	(2)	(0)	(0)	76	19.2
Do.....	.05	35	(31)	8	(2)	(0)	(0)	76	19.2
Do.....	.1	35	32	20	(10)	(0)	(0)	97	24.6
Do.....	.3	34	29	18	0	(0)	(0)	81	20.5
Do.....	.5	37	31	11	(1)	(0)	(0)	80	20.3
Do.....	1.0	37	33	0	(0)	(0)	(0)	70	17.7
Do.....	2.0	41	37	23	0	(0)	(0)	101	25.6
Do.....	3.0	50	46	40	29	17	5	187	47.3
Do.....	4.0	46	40	32	24	14	7	163	41.3
Do.....	5.0	49	39	34	27	20	10	179	45.3
Do.....	6.0	32	32	32	24	15	5	140	35.4

¹ At 3,420 minutes=5 percent; at 5,760 minutes=4 percent.

TABLE 11.—*Hydrometer data: Volclay and sodium tripolyphosphate*

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	91	88	89	88	85	86	527	99.1
.025	92	92	92	95	87	84	542	101.9
.05	92	92	91	91	88	85	539	101.3
.1	91	89	91	93	85	86	535	100.6
Synthetic Tri-County water								
0.0	98	98	100	90	(0)	(0)	386	72.6
.05	95	92	91	88	(0)	(0)	366	68.8
.1	98	98	94	87	46	3	426	80.1
.2	93	90	91	90	76	23	463	87.0
.3	97	94	92	91	77	59	510	95.9
.5	96	94	89	86	74	74	513	96.4
.75	92	89	88	90	(77)	68	504	94.7
1.0	93	90	90	88	84	74	519	97.6
1.25	94	92	91	91	90	80	538	101.1
1.5	97	95	94	92	90	84	552	103.8
1.75	97	96	92	88	88	84	545	102.4
2.0	94	92	92	92	87	85	542	101.9

TABLE 12.—*Hydrometer data: Volclay and sodium hexametaphosphate*

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	91	90	88	88	87	87	531	99.8
.025	94	91	93	93	94	87	552	103.8
.05	93	90	93	93	92	87	548	103.0
.1	93	89	93	93	89	89	546	102.6
Synthetic Tri-County water								
0.0	102	102	103	100	(0)	(0)	407	76.5
.05	94	91	90	86	(0)	(0)	361	67.9
.1	95	92	92	88	43	5	415	78.0
.2	95	93	90	88	83	8	457	85.9
.3	94	91	90	89	78	49	491	92.3
.5	92	92	89	85	80	66	504	94.7
.75	92	91	89	88	(84)	70	514	96.6
1.0	92	90	90	86	82	71	511	96.0
1.25	91	86	90	89	85	75	516	97.0
1.5	90	88	92	91	87	76	524	98.5
1.75	89	85	86	83	84	76	503	94.5
2.0	98	94	91	88	84	80	535	100.6

TABLE 13.—*Hydrometer data: Volclay and tetrasodium pyrophosphate*
[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0. 0	91	91	90	88	87	90	537	100. 9
. 025	95	93	93	93	94	86	554	104. 1
. 075	93	93	94	93	93	88	554	104. 1
. 1	93	92	94	92	89	90	550	103. 4
Synthetic Tri-County water								
0. 0	98	97	98	92	(0)	(0)	385	72. 4
. 05	92	91	90	84	(0)	(0)	357	67. 1
. 1	98	96	94	91	48	5	432	81. 2
. 2	94	91	90	86	79	41	481	90. 4
. 3	94	92	92	89	79	61	507	95. 3
. 5	94	92	91	90	89	79	535	100. 6
. 75	91	89	89	91	(83)	72	515	96. 8
1. 0	94	92	92	91	90	80	539	101. 3
1. 25	97	95	94	90	91	85	552	103. 8
1. 5	95	92	90	87	90	85	539	101. 3
1. 75	98	94	92	90	89	85	548	103. 0
2. 0	94	92	92	91	92	89	550	103. 4

TABLE 14.—*Hydrometer data: Kaolinite and sodium tripolyphosphate*
[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0. 0	94	93	88	79	58	50	462	102. 0
. 025	96	95	94	84	59	48	476	105. 1
. 05	98	96	90	82	64	49	479	105. 7
. 1	97	95	93	83	59	50	477	105. 3
Synthetic Tri-County water								
0. 0	100	51	5	5	(0)	(0)	161	35. 5
. 05	96	92	10	2	(0)	(0)	200	44. 2
. 1	100	99	28	4	0	1	232	51. 2
. 2	97	96	61	6	2	(0)	262	57. 8
. 3	98	96	84	13	1	(0)	292	64. 5
. 5	98	96	89	75	4	(0)	362	79. 9
. 75	100	94	89	80	(42)	14	419	92. 5
1. 0	100	98	90	79	61	49	477	105. 3
1. 25	96	94	91	81	63	50	475	104. 8
1. 5	100	97	90	82	63	49	481	106. 2
1. 75	100	98	89	87	61	48	483	106. 6
2. 0	98	96	92	80	57	50	473	104. 4

TABLE 15.—Hydrometer data: Kaolinite and sodium hexametaphosphate

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	91	90	84	80	56	50	451	99.6
.025	95	93	91	82	64	49	474	104.6
.05	93	91	91	81	63	51	470	103.8
.1	92	91	89	80	60	50	462	102.0
Synthetic Tri-County water								
0.0	100	64	6	4	(0)	(0)	174	38.4
.05	95	92	11	2	(0)	(0)	200	44.2
.1	100	96	21	6	0	(0)	223	49.2
.2	99	98	69	8	3	(0)	277	61.1
.3	97	94	86	16	1	(0)	294	64.9
.5	96	92	87	76	24	(6)	381	84.1
.75	95	93	90	76	(60)	48	462	102.0
1.0	94	90	86	74	59	47	450	99.3
1.25	94	91	87	76	62	50	460	101.5
1.5	94	92	88	78	62	49	463	102.2
1.75	96	90	84	72	58	47	447	98.7
2.0	92	91	78	69	56	46	432	95.4

TABLE 16.—Hydrometer data: Kaolinite and tetrasodium pyrophosphate

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	93	93	86	77	57	50	456	100.5
.025	95	93	89	71	64	48	460	101.7
.050	96	94	92	79	62	49	472	104.2
.1	93	91	90	79	59	51	463	102.7
Synthetic Tri-County water								
0.0	100	64	6	4	2	(0)	176	38.8
.05	95	90	6	2	(0)	(0)	193	42.6
.1	103	99	17	7	0	(0)	226	49.9
.2	99	97	32	2	2	(0)	232	51.2
.3	95	94	45	3	0	(0)	237	52.3
.5	98	97	86	15	1	(0)	297	65.6
.75	97	93	88	21	(11)	4	314	69.3
1.0	102	99	91	81	22	5	400	88.3
1.25	98	96	91	81	64	52	482	106.4
1.5	96	94	87	76	62	48	463	102.2
1.75	95	92	88	77	60	49	461	101.8
2.0	96	94	87	78	58	49	462	102.0

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TABLE 17.—Hydrometer data: Illite and sodium tripolyphosphate

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	94	90	81	64	38	28	395	100.0
.025	95	94	86	70	38	27	410	103.8
.05	97	93	83	67	40	25	405	102.5
.1	95	92	87	71	40	28	413	104.6
Synthetic Tri-County water								
0.0	101	94	40	4	(0)	(0)	239	60.5
.05	96	94	83	33	(3)	(0)	309	78.2
.1	100	96	88	30	2	(0)	316	80.0
.2	96	94	82	23	5	(0)	300	75.9
.3	97	95	75	3	1	(0)	271	68.6
.5	94	93	72	4	0	(0)	263	66.6
.75	94	90	75	10	(5)	0	274	69.4
1.0	98	92	80	59	6	0	335	84.8
1.25	96	92	79	66	40	25	398	100.8
1.5	95	90	80	66	40	28	399	101.0
1.75	98	92	78	61	40	26	395	100.0
2.00	96	89	76	67	40	31	399	101.0
2.25	100	96	84	70	51	35	436	110.4
2.50	100	98	90	77	50	36	451	114.2
2.75	96	95	90	73	50	38	442	111.9

TABLE 18.—Hydrometer data: Illite and sodium hexametaphosphate

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	90	90	80	66	38	28	392	99.2
.025	95	91	85	71	42	26	410	103.8
.05	93	90	85	67	42	27	404	102.3
.1	92	89	83	68	39	28	399	101.0
Synthetic Tri-County water								
0.0	102	97	43	4	(0)	(0)	246	62.3
.05	95	92	80	15	(0)	(0)	282	71.4
.1	98	94	65	6	1	(0)	264	66.8
.2	99	88	76	6	3	(0)	272	68.9
.3	97	94	44	2	2	(0)	239	60.5
.5	94	91	47	4	0	(0)	236	59.7
.75	95	92	72	4	3	1	267	67.6
1.0	94	90	69	6	4	3	266	67.3
1.25	96	95	83	48	5	3	330	83.5
1.5	98	93	82	64	6	4	347	87.8
1.75	94	89	76	60	34	5	358	90.6
2.0	98	92	81	68	37	7	383	97.0
2.25	95	93	82	65	47	11	393	99.5
2.50	100	98	90	76	47	11	422	106.8
2.75	95	93	83	71	48	37	427	108.1

TABLE 19.—Hydrometer data: Illite and tetrasodium pyrophosphate

[Ion saturation 78.8 percent sodium]

Grams deflocculent	Percentage in suspension after settling for the number of minutes indicated						Sum	Dispersion index
	1	4	19	60	435	1,545		
Distilled water								
0.0	94	94	84	66	38	30	406	102.8
.025	94	91	83	70	40	26	404	102.3
.05	91	89	80	65	40	27	392	99.2
.1	94	84	82	66	40	29	395	100.0
Synthetic Tri-County water								
0.0	97	91	33	4	(0)	(0)	225	57.0
.050	96	93	83	24	(6)	(0)	302	76.4
.1	101	100	81	11	1	(0)	294	74.4
.2	86	93	51	0	2	(0)	232	58.7
.3	97	91	21	0	-2	(0)	207	52.4
.5	96	90	2	0	0	(0)	188	47.6
.75	93	71	0	-1	-3	-5	155	39.2
1.0	99	34	8	2	-4	-6	133	33.7
1.25	101	88	50	30	7	3	279	70.6
1.5	98	91	60	38	17	8	312	79.0
1.75	99	93	66	46	21	10	335	84.8
2.0	99	65	56	50	22	14	306	77.5
2.25	96	86	78	65	41	25	391	99.0
2.50	102	102	94	76	47	30	451	114.2
2.75	97	97	89	73	44	32	432	109.4

FILTER-LOSS TEST OF CLAY SUSPENSIONS

By I. S. McQUEEN

A series of exploratory tests was conducted during the second year of the investigation to determine if there were significant differences in the sealing capacity of various clays with different deflocculents.

A standard operating procedure in the oil-well drilling-mud industry known as the filter-loss test or "filtration" provides information on the ability of a slurry to retain water inside of a drill hole during drilling operations (American Petroleum Institute, 1950, p. 7). The sediment lining in a canal is analogous to the filter cake in a drill hole.

The nature of the seal developed in a canal bottom by dispersed clays is not thoroughly understood. There are several possible mechanisms involved. Probably the seal easiest to develop is a surface seal or skin on the canal bottom. This type of seal, however, would be subject to erosion and would therefore be extremely temporary. The seal most permanent would be achieved by material that penetrates the soil mass and fills its interstices. The filling of cracks and other flow channels is an important factor in canal-sealing. Probably all of the above mechanisms are involved in an effective seal. The filter-loss test procedure was designed to define differences in pore-sealing as well as the relative permeability of the filter cake.

In the drill-mud filtration test, a quantity of 500 to 600 grams of mud is placed inside a cylinder on a disc of filter paper supported by a screen. The top of the cylinder is sealed and a pressure of 100 pounds per square inch is applied for 30 minutes. The character of the filter cake and the quantity of water extracted are measures of the effectiveness of the mud. The above procedure was modified for the current investigations because it was found that ordinary filter paper would not retain the dilute colloidal suspensions used.

Test procedure.—To retain colloidal-size particles an attempt was made to develop a barrier of greater depth and smaller pore size than ordinary filter paper. This was done by using glass beads, which are available in uniform sizes as small as 28 microns in diameter. In the chosen mixture 80 percent of the beads were between 20 and 70 microns in diameter. Uniform filter beds of these beads were formed by depositing a known weight of them in water on a filter paper in a Buechner funnel and consolidating the mass by alternately jarring the funnel and withdrawing the excess water with a partial vacuum. A filter paper was placed over the bed of beads to protect the bed from being disturbed by the suspensions being filtered and also to provide a means of removing the filter cake for testing the sealing brought about by particles that penetrated into the voids.

Results of the filter-loss tests are shown in table 20. The first four columns of table 20 describe the

TABLE 20.—Results of filter-loss tests

Sample	Colloid	Deflocculent	Water	Prerun cubic centimeters per hour	Cake development time in seconds	After run cubic centimeters per hour
1	Volclay	Sodium tripolyphosphate	Synthetic Tri-County with NaHCO ₃	447	7,740	-----
2	do	Sodium hexametaphosphate	do	473	8,790	-----
3	do	Sodium tripolyphosphate	Synthetic Tri-County with NaCl	411	7,380	125
4	do	Sodium hexametaphosphate	do	415	9,780	143
5	do	Sodium tripolyphosphate	Natural Tri-County	493	7,500	114
6	do	Sodium hexametaphosphate	do	522	8,760	115
7	Illite	Sodium tripolyphosphate	Synthetic Tri-County with NaCl	379	2,100	<100
8	do	Sodium hexametaphosphate	do	286	600	356
9	do	Tetra sodium pyrophosphate	do	336	1,680	293

suspension being tested. The next column shows the rate of movement of distilled water through the filter bed under a tension of 55 centimeters of water, prior to the application of the clay sample. The last column shows the rate of movement of distilled water through the filter bed under a tension of 55 centimeters of water, after application of the sample suspension and removal of the filter cake. This rate indicates the relative effectiveness of the suspension in sealing the soil matrix. The time required to develop the cake, by dewatering 100 cubic centimeters of the sample suspension with an applied tension of more than 800 centimeters, indicates the relative effectiveness of the sample in forming an impermeable cake.

The following characteristics may be inferred from the limited data obtained.

1. The filter cake formed using Volclay with sodium hexametaphosphate was consistently less permeable than the cake formed with Volclay and sodium tripolyphosphate.
2. There was no difference between sodium hexametaphosphate and sodium tripolyphosphate with Volclay in their "pore-sealing" ability.
3. The Volclay penetrated the filter bed and reduced its permeability to about one-third of its pretreatment permeability. The effect of illite on the permeability of the filter bed was variable; ranging from an increase in permeability to a reduction to about one-fourth.

The filter-loss experiments were discontinued because no well-defined differences in the effectiveness of the dispersants were evident and time would not permit a complete development of the method.

Limitations on filter-loss tests.—There are several serious limitations on the filter-loss test in its present stage of development. It is difficult to achieve consistently uniform filter beds. At present, the difference in permeability of two freshly prepared filter beds may be as great as the difference in the change in permeability

imposed on the filter beds by two samples with different deflocculating agents. The filter beds were not stable. One or two of them broke down and changed their basic permeability during the course of the tests. Sample 8 (table 20) is an example of this. The permeability of the filter bed increased 25 percent with the addition of the colloid. In this sample, the original packing of the beads seemed to be completely disturbed. Time would not permit further work on this filter-loss test to eliminate these limitations so the tests were discontinued.

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